AN ABSTRACT OF THE THESIS OF

Aimee B. Carangal for the degree of **Master of Science** in **Chemical Engineering** presented on **September 6, 1994**.

Title: The Release of NO During Black Liquor Pyrolysis.

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Abstract approved : _____

Dr. Kristiina Iisa

NO_x formation in kraft recovery boilers has become increasingly important as more stringent environmental regulations are being enforced. The fuel NO_x mechanism has been found to be the leading NO formation pathway in kraft recovery boilers. However, there has been relatively little information available on the rate of fuel NO formation during black liquor combustion processes. The purpose of the study was to examine fuel NO formation mechanisms during black liquor pyrolysis -- one of the processes occurring during the devolatilization stage of the combustion process.

The release of NO during black liquor pyrolysis in N_2 was investigated using a laminar entrained flow reactor (LEFR) at residence times ranging from 0.5 to 4.5 seconds. The operating furnace temperatures were between 600 °C - 1100 °C. The NO and NH_3 released and the nitrogen retained in the char were measured.

Results indicated that 35 to 65 % of the original fuel nitrogen volatilized depending on the furnace temperature and residence time. The rate of nitrogen release was found to be enhanced by temperature. NO and NH_3 were formed; however, the NH_3 released was not successfully measured. NO was formed due to the oxidation of NH_3 or other N intermediates.

A closer look at the release of NO during black liquor pyrolysis at 700 °C, 800 °C and 900 °C showed that NO formation increased with increasing temperature and

residence time. NO formation started at shorter residence times for higher temperatures. NO levels initially increased with residence time and eventually reached a maximum. The maximum fuel N conversion to NO was about 20 %. The maximum occurred because the NO destruction mechanisms were dominant at longer residence times.

The nitrogen content in the char decreased with increasing temperature and residence time. However, the relative weight of the char nitrogen to char remained constant. The weight percentage of nitrogen in the char was approximately equal to the original nitrogen content in the black liquor. A comparison between the carbon content and nitrogen content in the char indicated that the carbon evolution rate was greater than the nitrogen evolution rate during char reactions.

The Release of NO
During Black Liquor Pyrolysis

by

Aimee B. Carangal

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed September 6, 1994

Commencement June, 1995

Master of Science thesis of **Aimee B. Carangal** presented on **September 6, 1994**

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ACKNOWLEDGMENTS

I would like to express my appreciation to Dr. Kristiina Iisa and Dr. William James Frederick for their help and encouragement to achieve this degree. I give special recognition to my major professor, Dr. Kristiina Iisa, for her generous help, guidance and support. She had given valuable suggestions without which this research work and thesis could never have been successful.

I would also like to express my gratitude to the following people for their help and cooperation -- Scott Sinquefield, Victor Reis, Narongsak Jivakanun, Viboon Scricharoenchaikul, Kaj Wag, and Yan Lu. I give my special thanks to my co-workers, Rungsun Pianpucktr and Sheng-Liang Wu, the other "NO_x people" of the group, for sacrificing their time and putting much effort in helping me gather data for this study.

Finally, I would like to acknowledge the following sponsors -- the U.S. Department of Energy, ABB Combustion Engineering, Ahlstrom Recovery Inc., and Gotaverken Energy Systems.

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LIST OF NOMENCLATURE

BL_{actual}	amount of actual black liquor fed into LEFR, g
BL_{feed}	amount of black liquor feed, g
$char_{ex}$	amount of char collected during the experiment, g
$char_f$	amount of char collected during the flushing routine, g
$char_{total}$	the sum of $char_{ex}$ and $char_f$, g
d_i	inside diameter of the injector, cm
d_r	inside diameter of the reactor, cm
l	reactor pathlength, inch
N_{char}	amount of char-N, g
$NH_{3\,total}$	total NH_3 absorbed in the HCl solution, mg
N_{in}	fuel nitrogen content of the black liquor, g
NO_0	NO concentration reading at zero NO, ppm
NO_{calib}	calibration gas concentration, ppm
$NO_{display}$	NO voltage reading displayed in data acquisition program, V
NO_e	NO concentration reading from data acquisition program, ppm
NO_{ei}	NO concentration reading at i^{th} time step, ppm
NO_i	actual NO concentration at i^{th} time step, ppm
NO_{mean}	average NO concentration, ppm
NO_r	average concentration reading for NO calibration gas, ppm
NO_{total}	total NO detected by NO-NO_x meter during experiment, ppm·sec
P	reactor pressure, atm
R	gas constant, $\frac{\text{li atm}}{\text{mol K}}$
t_a	hour reading from data acquisition, hr
t_b	minute reading from data acquisition, min

LIST OF NOMENCLATURE (continued)

t_c	second reading from data acquisition, sec
t_d	hundredth of a second reading from data acquisition, 1/100 sec
T_f	furnace temperature, K
t_i	time at i^{th} data acquisition reading, sec
T_{room}	room temperature, K
t_{run}	total running time, sec
u_i	velocity of primary gas, cm/min
u_t	velocity of total gas, cm/min
V_e	effective reactor volume, cm^3
V_r	total reactor volume, cm^3
$V_{scrubber}$	total gas flow into the HCl solution, l
V_{Stotal}	volume of the HCl scrubber solution, ml

SYMBOLS

γ	char yield, %
τ_{ave}	average residence time, sec
τ_p	residence time based on primary gas flow, sec
τ_t	residence time based on total gas flow, sec
ν_{pf}	primary gas flow rate at furnace temperature, l/min
ν_{pr}	primary gas flow rate at room temperature, l/min
ν_{qr}	quench gas flow rate at room temperature, l/min
ν_{sr}	scrubber gas flow rate at room temperature, l/min
ν_{tf}	total gas flow rate at furnace temperature, l/min
ν_{tr}	total gas flow rate at room temperature, l/min

The Release of NO During Black Liquor Pyrolysis

CHAPTER 1
INTRODUCTION

1.1 Nitrogen-containing Compounds -- An Environmental Problem

One of the leading environmental concerns is air pollution. Air pollutants are defined as contaminants present in the atmosphere in such quantities and of such duration that tend to be injurious to any biological life and its welfare (Wark and Warner, 1981). They unreasonably interfere with the enjoyment of life and property. Nitrogen-containing compounds, particularly oxides of nitrogen, are considered as pollutants. Such compounds include N_2O (nitrous oxide), NO (nitric oxide), N_2O_3 (dinitrogen trioxide), NO_2 (nitrogen dioxide), N_2O_5 (dinitrogen pentoxide) and the unstable NO_3 (nitrogen trioxide). Only NO, NO_2 and N_2O are present in significant amounts and are thus of great importance for current research. The sum of NO and NO_2 is defined as NO_x.

The atmospheric distribution of nitrogen oxides is non uniform. About 90 % of nitrogen oxides present in the atmosphere is produced by natural sources such as natural bacterial action, natural combustion and lightning (Seinfeld, 1986). **Figure** 1.1 illustrates the atmospheric cycles of nitrogen compounds. As a result of this cycle, the average background concentration of nitrogen oxides in nonpolluted environments is 1 ppb (Wark and Warner, 1981). However, nitrogen oxide concentrations in localized urban areas tend to far exceed the clean air background concentrations. The approximate concentrations of nitrogen-containing species in the clean troposphere and polluted urban air are compared in **Table** 1.1. The primary anthropogenic source of NO_x emissions is the combustion process, more than 50% of which is due to fuel combustion in stationary sources, while the rest is due to transportation, industrial processes, and solid waste disposal (Wark and

Warner, 1981). Because ambient concentrations of N_2O are considerably below the threshold for a biological effect, NO_x emissions are given greater importance in today's environmental issues.

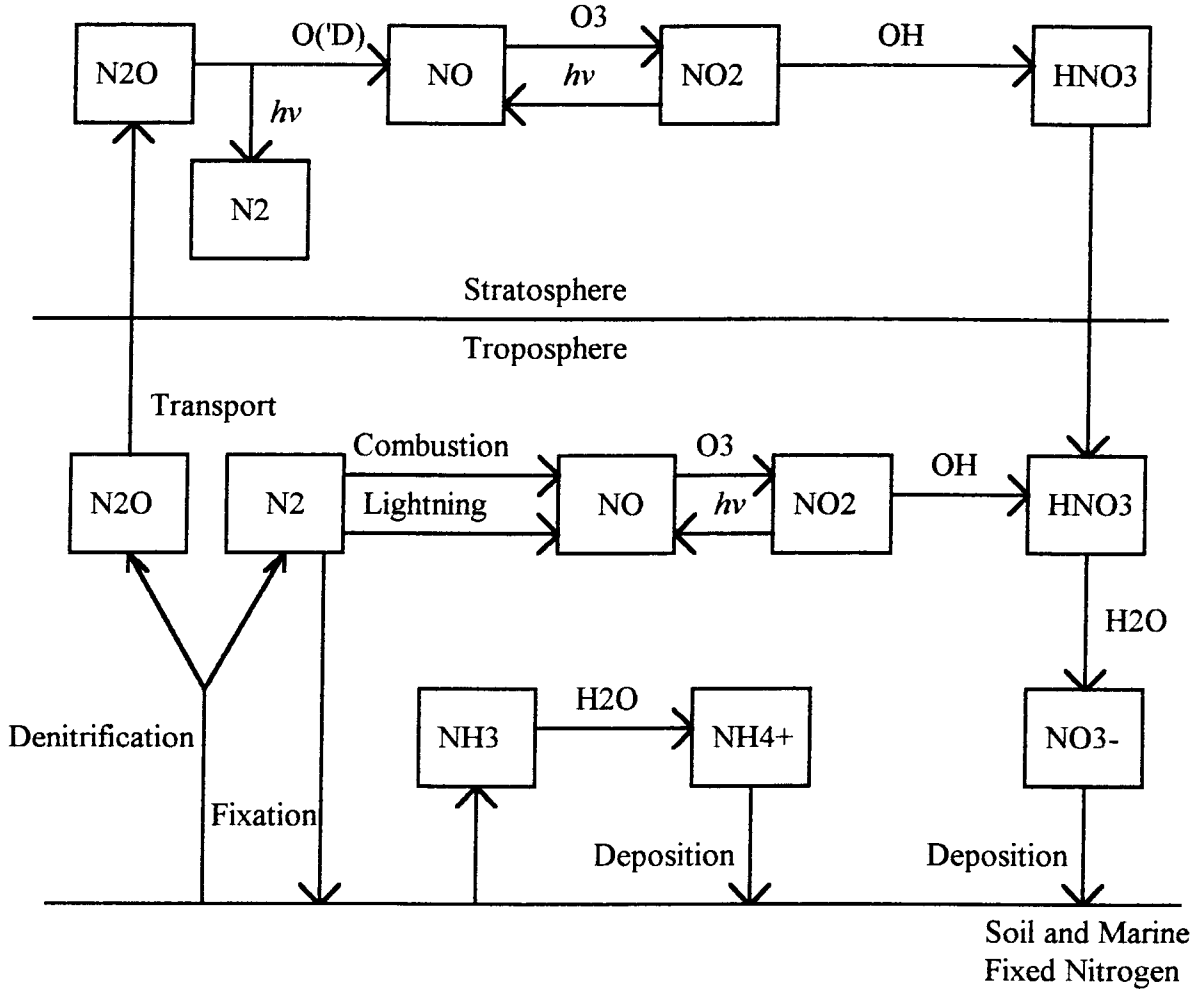


Figure 1.1. Schematic Diagram of the Atmospheric Cycles of Nitrogen Compounds (based on Stedman and Shetter, 1983)

Table 1.1. Comparison of the Concentration of Nitrogen-containing Compounds in a Clean Troposphere and Polluted Urban Air (Seinfeld, 1986)

Species	Clean Troposphere	Polluted Urban Air
NO (nitric oxide)	0.01 - 0.05 ppb	50-750 ppb
NO_2 (nitrogen dioxide)	0.1 0.5 ppb	50 - 250 ppb
HNO_3 (nitric acid)	0.02 - 0.3 ppb	3 - 50 ppb
NH_3 (ammonia)	1 ppb	10 - 25 ppb
HNO_2 (nitrous acid)	0.001 ppb	1 - 8 ppb
$CH_3C(O)O_2NO_2$ (peroxyacetyl nitrate (PAN))		5 - 35 ppb
NMHC (non-methane hydrocarbons)		500 - 1200 ppb

NO_x emissions have short and long range effects. NO is a colorless gas and its ambient concentration is well below the threshold to be considered harmful to human health (Wark and Warner, 1981). Its average lifetime in the troposphere is short, only minutes or even seconds, since NO is rapidly oxidized to NO_2 by the following reaction

$$2\ NO + O_2 \Rightarrow 2\ NO_2$$

NO_2 is a reddish brown gas and is visible in sufficient amounts (1 ppm of NO_2 would probably be detected by the eye). NO_2 is known to for its respiratory effects. It may cause eye and nose irritation, as well as slow plant growth.

The acid rain problem can be attributed, in part, to the presence of NO_x in the atmosphere. On the average, NO_x contributes about 30 % to the acidity of rain, while the rest is due to SO_x (Elsom, 1992). NO_2 is hydrolyzed to nitric acid (HNO_3) in the atmosphere via a series of reactions that also involves intermediate reactions with carbon monoxide (CO), another air pollutant.

$$NO_2 + OH \Rightarrow HNO_3 \text{ (several steps)} \qquad (1.1)$$

This in turn is precipitated as nitrates. These return to the earth's surface and act as fertilizer. However, excessive amounts of acidic nitrogen in the soil can lead to leaching of important nutrients such as Mg^{+}, Ca^{2+}, and K^{+} into the groundwater. The yellowing of the needles and leaves of trees and plants may be due to magnesium and calcium deficiency as a secondary effect of nitrogen deposition. Acid rain also causes acidification of lakes and other surface waters causing fish damage. The cumulative deposition on metal surfaces can cause corrosion. Stoneworks in many cities are being eroded away, although the effect of NO_x is ten times less pronounced than that of SO_x. The effects of acidic deposition on metal, stone, ceramics, and glass are especially seen in urban areas where NO_x concentrations in the atmosphere are high. In recent years, it has been observed that the overall contribution of NO_x to the acidity of rain is increasing (Elsom, 1992).

NO_x is also an active compound in photochemical smog formation. Photochemical smog is a mixture of reactants and products that results from the interaction of organics with the oxides of nitrogen. When NO and NO_2 are present in the atmosphere, the formation of ozone occurs.

$$NO_2 + h\nu \Rightarrow NO + O \qquad (1.2)$$

$$O + O_2 + M \Rightarrow O_3 + M \qquad (1.3)$$

M is either N_2 or O_2 or another molecule that can absorb the excess vibrational energy and stabilize the O_3. **Reaction** 1.3 is the only significant source of ozone in the atmosphere. However, little O_3 is formed via the reactions above since it reacts rapidly with NO to regenerate NO_2.

$$O_3 + NO \Rightarrow NO_2 + O_2 \qquad (1.4)$$

The O_3 produced in the troposphere is a "greenhouse gas" and is a contributor in the "greenhouse effect". The greenhouse gases in the atmosphere allow short-wave (incoming) solar energy to pass through, but absorb long-wave (outgoing) infrared

radiation that would otherwise be lost to space. The atmosphere is warmed by this process and the radiation is reradiated towards the earth's surface causing global warming.

Finally, NO_x in the upper troposphere/stratosphere can react with and thus contribute to the depletion of stratospheric O_3. The stratospheric O_3 is responsible for absorbing the solar radiation and shielding the earth from harmful uv rays. O_3 is formed in the stratosphere as follows

$$O_2 + h\nu \Rightarrow O + O \qquad (1.5)$$

$$O + O_2 + M \Rightarrow O_3 + M \qquad (1.6)$$

NO_x is responsible for 70 % of the natural ozone destruction rate in the stratosphere (Seinfeld, 1986). The conversion of N_2O to NO is the major source of NO in the stratosphere. The NO_x from the troposphere does not reach the stratosphere and thus, does not contribute to ozone depletion. However, the N_2O has an atmospheric lifetime of 150 years and is able to reach the stratosphere due to atmospheric movement. Although, almost all of the N_2O is converted by uv light into N_2 and O, about 1% reacts with excited oxygen atoms, $O(^1D)$, formed by the action of uv radiation on O_3, to yield NO (Seinfeld, 1986).

$$O(^1D) + N_2O \Rightarrow NO + NO \qquad (1.7)$$

Ozone destruction is provided by presence of NO_x by the following reactions

$$O + NO_2 \Rightarrow NO + O_2 \qquad (1.8)$$

$$NO + O_3 \Rightarrow NO_2 + O_2 \qquad (1.9)$$

The depletion of ozone may affect the distribution of solar heating and result in the change of climate that could affect agriculture in many areas of the world. Furthermore, the uv radiation is a major cause of human skin cancers and possibly also leads to the suppression of the human immune system. Nevertheless, the increased amount of uv radiation will cause increased photolysis of N_2O and thus a decrease in the greenhouse activity of this gas (Sinclair, 1990).

The NO_x in the stratosphere is removed by the formation of HNO_3 (reaction 1.1) in the lower stratosphere. The HNO_3 is carried downward to the troposphere where it is removed by rain.

1.2 Black Liquor and Black Liquor Combustion -- A Source of NO_x

Three major constituents of wood are cellulose, hemicellulose, and lignin. In the process of chemical pulping, the lignin in the wood is dissolved with minimal negative effect on the cellulose fibers. This can be achieved by using sufficiently high sulfidity in the kraft process in which a mixture of sodium hydroxide and sodium sulfide is added. With the process, 90 to 95% of the lignin is dissolved (Brannland, 1991).

Black liquor is the material that is recovered after washing the resulting wood fiber from the pulping process. It consists of all inorganic cooking chemicals along with the lignin and other organics separated from the wood. It initially contains 15% dry solids in water. The raw black liquor is fed into a series of evaporators, normally five to six at successively decreased pressure. The solids content of the resulting black liquor is about 60 to 80% (Adams and Frederick, 1988; Brannland, 1991). Black liquor solids (BLS) include C, H, O, Na, K, S, Cl, and inerts (*i.e.*, Si, Al, Fe, Ca, etc.). **Table** 1.2 shows a typical sample analysis of BLS.

Table 1.2. Sample Analysis of Kraft Black Liquor (Concentrator Product) (Adams and Frederick, 1988)

Element	wt.% BLS
carbon (C)	39.0 %
hydrogen (H)	3.8 %
oxygen (O)	33.0 %
sodium (Na)	18.6 %
potassium (K)	1.2 %
sulfur (S)	3.6 %
chloride (Cl)	0.6 %
inerts (Si, Al, Fe, Ca, *etc.*)	0.2 %

higher heating value (HHV) = 15,350 kJ/kg BLS
lower heating value (LHV) = 12,180 kJ/kg BLS
solids content = 65 %

Black liquor is burned in large units called kraft recovery boilers, the purpose of which is to recover the inorganic cooking chemicals and to generate steam for the pulping mill. **Figure** 1.2 provides a general design for a kraft recovery boiler. The black liquor fuel is first mixed with make-up chemicals and a substantial amount of recycle particulates from the electrostatic precipitator, and boiler bank and economizer ash hoppers. **Table** 1.3 provides a sample analysis of the make-up chemical, usually saltcake (Na_2SO_4), used in the process. The mixture is then heated to reduce its viscosity thus, improving its spray characteristics. It is fed into the furnace through a set of nozzles called liquor guns. The organic material is burned to produce energy for steam generation, while the inorganic material (mostly Na compounds) forms a liquid smelt and exits through smelt spouts in the bottom of the char bed.

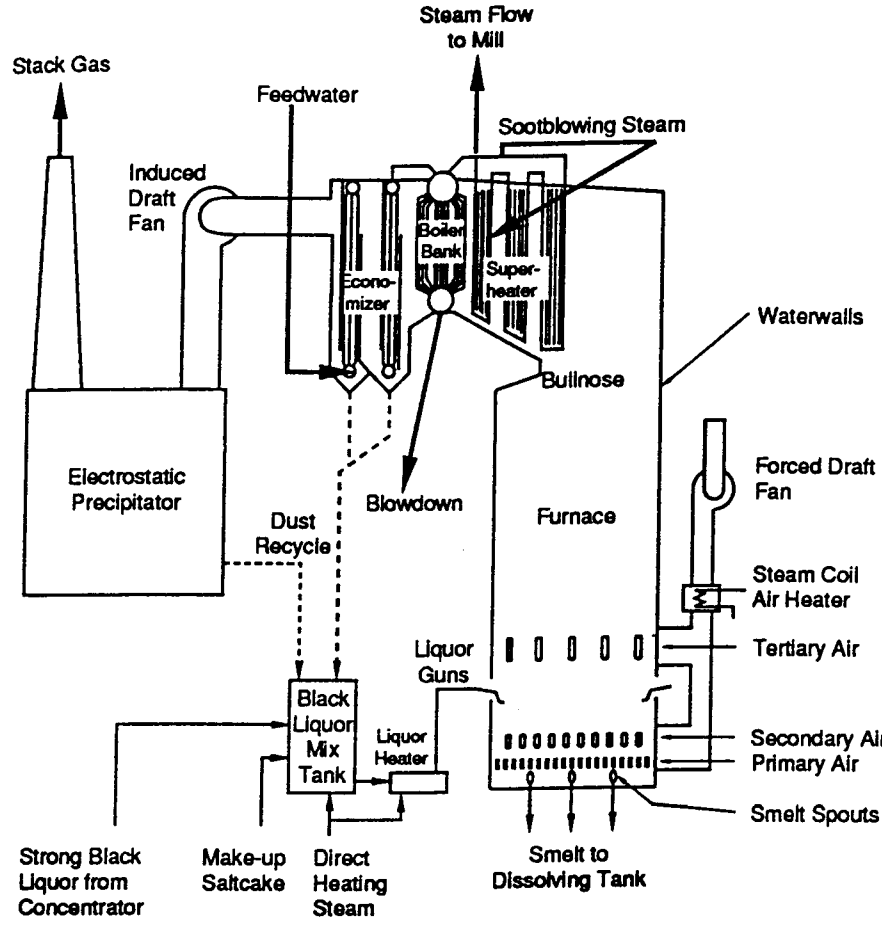


Figure 1.2. A Kraft Recovery Furnace
(Adams and Frederick, 1988)

Table 1.3. Sample Analysis of Make-up Saltcake (Adams and Frederick, 1988)

Element	wt.% BLS
sodium (Na)	32.4 %
sulfur (S)	22.4 %
oxygen (O)	44.8 %
chloride (Cl)	0.3 %
inerts (Si, Al, Fe, Ca, *etc.*)	0.1 %

1.3 Motivation of the Study

Black liquor, being the 6th leading fuel in combustion in the world, is a source of NO_x emissions. The NO_x emission levels depend on the nitrogen content of BLS, the type of furnace and operating conditions used. The nitrogen content of kraft black liquors range from 0.04 to 0.26 weight percent (wt. %) of dry BLS, with an average of 0.11 wt.%. Twenty percent of this amount accounts for the typical levels of NO_x emission in recovery boilers, approximately 25 to 120 ppm (@ 8% O_2) (Nichols *et al.*, 1992). The contribution of recovery boilers to total NO_x levels in the atmosphere is small as compared to coal, oil and gas combustion. However, as environmental concerns continue to increase, Environmental Protection Agency (EPA) standards for NO_x emissions are becoming more stringent.

The Clean Air Act of 1970 stated that the national ambient air quality standard (NAAQS) for NO_x is 0.053 ppm on an annual arithmetic mean basis. The Clean Air Act of 1970 was set to create a healthy atmosphere. However, it was not achieved. **Table** 1.4 shows the ambient air pollution concentrations of NO_2 (and ozone) in selected cities in the U.S. in 1988 (Elsom, 1992). Although most U.S. cities had NO_2 levels less than the 0.053 ppm, the ozone levels were higher than the NAAQS of 0.12 ppm on an hourly basis. The Clean Air Act Amendments of 1990 required the control of pollutants from various industrial processes in ozone nonattainment areas. These areas are those that violate the air quality standards for ozone. The control of NO_x (and volatile organic compounds, "VOC") - a precursor to ozone - is required in these areas. **Tables** 1.5 and 1.6 show the requirements for controlling these pollutants as stated in Title I of the Clean Air Act Amendments of 1990 (Mehta, 1994).

The impact of the new regulations to the pulp and paper industry is expected to cost about US$ 20 billion over the next ten years (Mehta, 1994). Current research in NO_x emissions from black liquor combustion is becoming increasingly important in the pulping

industry in order to be able to further comply with the new stated regulations. Some conventional NO_x control technologies have been a question in some researches. However, difficulties arise due to the complexity of a kraft recovery boiler design and operation (refer to **Chapter 3**). Furthermore, the capital costs and operating costs may be very high (Wood, 1994). Therefore, the main motivation of this project was the need to further examine NO_x formation mechanisms during black liquor combustion processes as this is the preliminary measure to determine the best NO_x emission control method.

Table 1.4. Ambient Pollution Concentrations of NO_2 and O_3 in Selected US Cities (US EPA, 1990)

Standard metropolitan statistical area	**Nitrogen Dioxide (NO_2) annual arithmetic mean (ppm)**	**Ozone (O_3) 1 h second maximum daily value (ppm)**
New York City	0.041	0.18
Los Angeles - Long Beach	0.061	0.33
Chicago	0.032	0.22
Philadelphia	0.039	0.20
Detroit	0.023	0.16
Washington, D.C.	0.030	0.18
Dallas	0.021	0.13
Houston	0.028	0.22
Boston	0.033	0.17
Nassau-Suffolk	0.035	0.16
St. Louis	0.025	0.15
Pittsburgh	0.030	0.16
Baltimore	0.034	0.19
Minneapolis - St. Paul	0.020	0.11
Atlanta	0.030	0.17
NAAQS	***0.053***	***0.012***

Table 1.5. Ozone Nonattainment Area Requirements (Mehta, 1994)

New source or Major modification	Existing source
Must meet lowest achievable emission rates (LAERs)	Must apply reasonably available control technology (RACT)
Requires offsetting emissions	Application of RACT now required for both VOC and NO_x emissions
Source owner must show statewide compliance	Requirements extended for very small sources, e.g. serious area: 50 tons/yr extreme area: 10 tons/yr

Table 1.6. Major Source/Major Modification Thresholds (Mehta, 1994)

Pollutant	Major source [b] tons/yr	Major modification net increase, [b] tons/yr	Offset ration, minimum
VOC/NO_x [a]			
I. Marginal	100	40	1.10 to 1
II. Moderate	100	40	1.15 to 1
III. Serious	50	25	1.20 to 1
IV. Severe	25	25	1.30 to 1

[a] VOC and NOx emissions are to be considered separately to determine whether a source is subject to permit requirements.
[b] *De minimus* values

1.4 Objectives of the Study

The study focused on the measurement of NO and NH_3 released and the nitrogen retained in the char during black liquor pyrolysis as a function of temperature and residence time. Black liquor pyrolysis is one of the processes occurring during the devolatilization stage of the black liquor combustion process. The method employed was rapid pyrolysis in a laminar entrained flow reactor (LEFR). The objectives of the study are

- to establish the feasibility of measurements in the kinetic evolution of nitrogen in black liquor during the pyrolysis stage in the LEFR
- to determine the split between the nitrogen released as gas (volatile-N) and that which remained in the char (char-N)
- to examine the conversion of fuel nitrogen to NO and NH_3 during the pyrolysis
- to obtain a general trend in nitrogen evolution in black liquor pyrolysis as a function of temperature and residence time

1.5 Thesis Review

This thesis report first explains the NO_x formation mechanisms in combustion processes in **Chapter 2**. It then provides extensive literature review in **Chapter 3** on black liquor combustion, with general attention brought to NO_x formation and depletion in recovery furnaces. **Chapter 4** explains the operations of the equipment used in this study, particularly that of the laminar entrained flow reactor and the chemiluminecence NO/NOx analyzer. It also illustrates the procedure used in the experiments and analysis. Results are presented in **Chapter 5** and discussed in **Chapter 6.** The conclusions for the study are summarized in **Chapter 7**. Finally, necessary recommendations and future work are briefly discussed in **Chapter 8**.

Experimental and analytical data are presented in **Appendix A**. The experimental procedure used in all the runs is outlined in **Appendix B** while analytical procedures are presented in **Appendix C**. These procedures are too detailed to be included in **Chapter 4** of the report. The relevant equations and the summary of analytical results are presented in **Appendix D**. Finally, **Appendix E** presents some valuable results during the preliminary experiments.

CHAPTER 2
A REVIEW OF NO_x FORMATION MECHANISMS IN COMBUSTION PROCESSES

The principles of NO_x emissions control in combustion are best understood when the principles of NO_x formation are known. Usually, about 90 - 95 % of the NO_x formed in combustion processes is NO; only a small fraction is NO_2 (Sloss, 1992). The formation of NO, and subsequently NO_2, occurs by three independent mechanisms: thermal NO, fuel NO and prompt NO.

2.1 Thermal NO

This mechanism, which was first described by Zeldovich in 1946, involves the oxidation of nitrogen present in the combustion air. It is due to the thermal fixation of atmospheric molecular nitrogen by oxygen atoms. At high temperatures, free oxygen atoms are produced by the dissociation of O_2 molecules or by an attack of a free radical. This begins the simple chain mechanism, also known as the Zeldovich mechanism.

$$O + N_2 \underset{-1}{\overset{1}{<=>}} NO + N \qquad (2.1)$$

$$N + O_2 \underset{-2}{\overset{2}{<=>}} NO + O \qquad (2.2)$$

The rate constants for the thermal NO production are given in **Table** 2.1. The first step (**reaction** 2.1) has a high activation energy and it is the rate-limiting step. This high activation energy results from the breaking of the nitrogen triple bond. The Zeldovich mechanism is very temperature sensitive, hence the name "thermal" NO.

In fuel-rich conditions, the second step is less important than in fuel-lean combustion. The Zeldovich mechanism is extended to account for the major sink for N in

fuel-rich combustion. The third reaction step involves the reaction of the hydroxyl radical (OH) with N.

$$N + OH \underset{-3}{\overset{3}{<=>}} NO + H \qquad (2.3)$$

The rate constants for the third step are also shown in **Table** 2.1.

Table 2.1. Rate Constants for Thermal NO Formation (Flagan and Seinfeld, 1988)

Reaction number	**rate constant, *k*** **(m^3 mol^{-1} s^{-1})**
1	$1.8 \times 10^8 \exp(-38{,}370 / T)$
-1	$3.8 \times 10^7 \exp(-425 / T)$
2	$1.8 \times 10^4 T \exp(-4{,}680 / T)$
-2	$3.8 \times 10^3 T \exp(-20{,}820 / T)$
3	$7.1 \times 10^7 \exp(-450 / T)$
-3	$1.7 \times 10^8 \exp(-24{,}560 / T)$

T = reaction temperature in K

From the first and second step of the Zeldovich mechanism, the overall reaction can be expressed as

$$N_2 + O_2 <=> 2\,NO \qquad (2.4)$$

The reaction is highly endothermic, with standard heat of formation [ΔH_r^o (298 K)] equal to 90.4 kJ mol^{-1}(Flagan and Seinfeld, 1988). From **reactions** 2.1 and 2.2, the rate of thermal NO formation is given by

$$\frac{d[NO]}{dt} = k_1[N_2][O] - k_{-1}[N][NO] + k_2[N][O_2] - k_{-2}[NO][O] \qquad (2.5)$$

where k_i is the rate constant for reaction i given in **Table** 2.1. A simplified expression can be obtained to approximate the rate of thermal NO formation. The following assumptions are relevant:

- The O_2 dissociation reaction, $1/2\ O_2 <=> O$, is at equilibrium. Thus,

$$[O] = K_o [O_2]^{1/2} \tag{2.6}$$

where K_o is the equilibrium constant for O_2 dissociation reaction (Flagan and Seinfeld, 1988),

$$K_0 = K_{p0} (RT)^{-1/2} \tag{2.7}$$

and

$$K_{p0} = 3030 \exp\left(\frac{-57,830}{T}\right) \ \text{atm}^{-1/2} \qquad \text{T is in K} \tag{2.8}$$

- Atomic nitrogen formation is at steady state

$$\frac{d[N]}{dt} = k_1[N_2][O] - k_{-1}[N][NO] - k_2[N][O_2] + k_{-2}[NO][O] \tag{2.9}$$

where an expression for [N] can be derived

$$[N] = \frac{[O](k_1[N_2] + k_{-2}[NO])}{k_{-1}[NO] + k_2[O_2]} \tag{2.10}$$

- Finally, the $[O_2]$ is significantly greater than [NO]; *i.e.*, $[O_2] >> [NO]$ Similarly, $k_2[O_2] >> k_{-1}[NO]$ and **eqn.** 2.10 is simplified to

$$[N] = \frac{[O](k_1[N_2] + k_{-2}[NO])}{k_2[O_2]} \tag{2.11}$$

Substitution of **eqns.** 2.6 and 2.11 into **eqn.** 2.5 and further simplifications lead to an expression for the thermal NO formation rate

$$\frac{d[NO]}{dt} = 2K_o k_1 [N_2][O_2]^{1/2} \frac{K_o k_{-1} k_{-2} [NO]^2}{k_2 [O_2]^{1/2}} \tag{2.12}$$

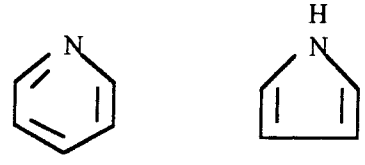
The maximum NO formation rate can be obtained by considering only the forward reactions

$$\frac{d}{dt}[NO] = 2K_o k_1 [N_2][O_2]^{1/2} \qquad (2.13)$$

It is evident from the rate expression given in **eqn.** 2.13 that the key factors that determine the extent of thermal NO formation are temperature, oxygen concentration, and residence time.

2.2 Fuel NO

This mechanism occurs due to the oxidation of nitrogen in the fuel, designated as "fuel N". The nitrogen in fossil fuels is usually in the form of pyridine and pyrrole groups (Flagan and Seinfeld, 1988).



pyridine pyrrole

During pyrolysis, the molecules undergo ring schism and devolatilization of fuel N occurs. Pyridinic groups are more stable than the pyrrolic groups; thus, a higher temperature is required for nitrogen devolatilization (Nelson *et al.* 1992).

The nitrogen in kraft black liquors has been found to contain heterocyclic nitrogen compounds (Niemela, 1990). On the other hand, an analysis of lignin, the major component of the kraft black liquors, showed that the nitrogen content was almost exclusively amino acid nitrogen (Dill *et al.*, 1984). With these results, the nitrogen in kraft black liquors may be in the form of heterocyclic compounds and/or amines. Thus, the

mechanism of nitrogen devolatization in black liquor combustion may be different from that in the combustion of other fuels.

The complete fuel NO mechanism has not been fully determined (Bowman, 1991). However, in coal combustion, it has been accepted that reactions proceed as illustrated in **Figure** 2.1. Fuel N is rapidly converted to hydrogen cyanide (HCN) via a single step reaction (Bowman, 1991). This initiates several homogeneous reactions converting HCN into other nitrogen containing intermediates and radicals such as CN, NH_i, N. These intermediates are then converted to NO by attack of oxygen-containing species or to N_2 by attack of either NH_i species or NO itself.

Fuel NO formation is strongly dependent to oxygen concentration and fuel nitrogen content and weakly dependent on the flame temperature and the nature of organic nitrogen compound (Campbell *et al.*, 1992).

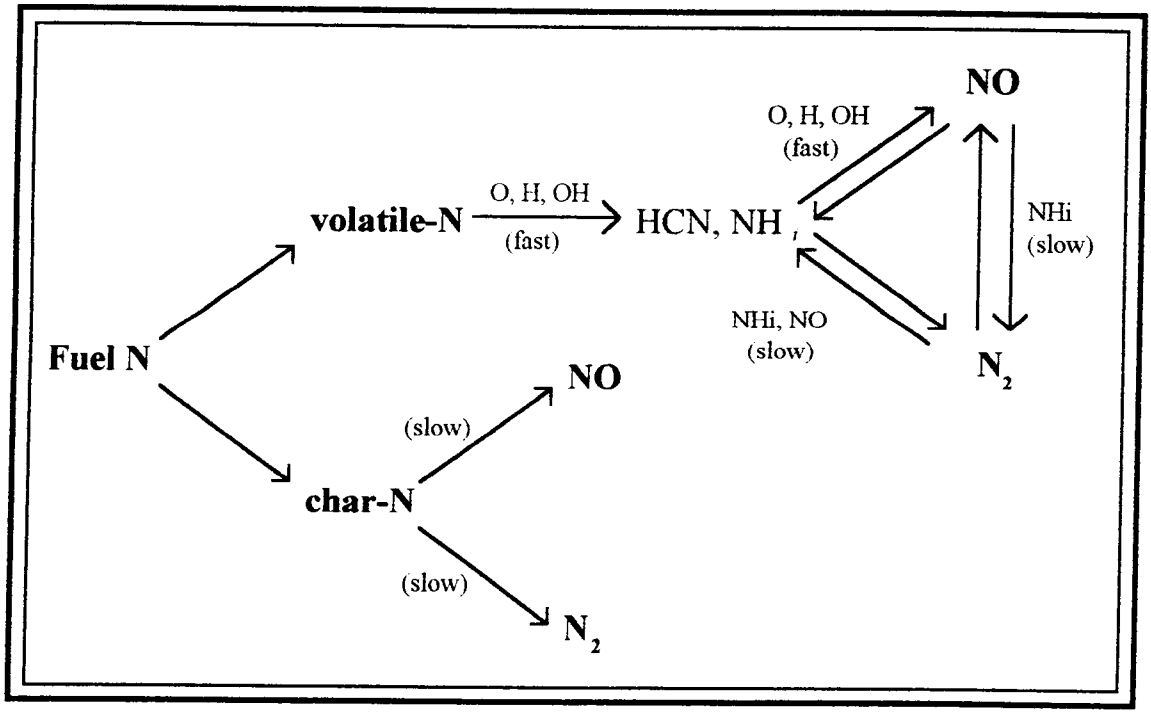


Figure 2.1. A Schematic Diagram of Fuel NO Formation Mechanism
(based on Flagan and Seinfeld, 1988)

Not all fuel nitrogen is evolved during devolatilization. Some remains in the char, hence the name "char-N". The nitrogen remaining in the char can be heterogeneously oxidized to form NO (refer to **Figure** 2.1). Char nitrogen contribution to fuel NO in pulverized coal combustion is significant (Pershing and Wendt, 1976). In coal char combustion, the conversion efficiency of char N to NO is found to be nearly independent of fuel N content or oxygen concentration and to be approximately 35 - 65 % (de Soete, 1990). The nitrogen is evolved from the char mainly as N_2 and NO as shown in **Figure** 2.1.

2.3 Prompt NO

The prompt NO mechanism was first identified by C.P. Fenimore in 1971. It involves the attack of a hydrocarbon free radical on N_2 in air and formation of HCN.

$$CH + N_2 \Rightarrow HCN + N \qquad (2.14)$$

This is followed by the oxidation of HCN to NO similar to those reactions occurring in the fuel NO formation. The reaction occurs at low temperatures, fuel rich conditions, and short residence times. NO formation via this mechanism is considered negligible in most combustion process since the rate of oxidation of the fuel is relatively faster than the prompt NO formation (Flagan and Seinfeld, 1988). However, as NO levels are reduced by applying NO control technologies, the relative importance of prompt NO may be expected to increase.

CHAPTER 3
NO_x FORMATION IN BLACK LIQUOR COMBUSTION – LITERATURE REVIEW

3.1 Black Liquor Combustion

Several studies are currently being done to characterize black liquor combustion. The objectives of these studies are similar to those in coal combustion research. The basic processes in black liquor combustion are similar to those in other solid fuels combustion. However, there may be differences in the combustion behavior since there are some important characteristics that make black liquor different from other fuels. First, a major constituent in black liquor is the low melting point inorganics such as sodium compounds that act as a diluent for the combustible organic portion of the black liquor. The inorganics are responsible for fume and smelt formation and they enhance the reactivity of the black liquor char. Second, the black liquor undergoes substantial swelling to a maximum volume factor of 20 - 50 depending on the liquor type during combustion (Frederick *et al.*, 1991). This can affect the internal and external transport processes important in the combustion process (Adams and Frederick, 1988).

The four stages in black liquor combustion are drying, devolatilization, char burning, and smelt coalescence shown in **Figure** 3.1.

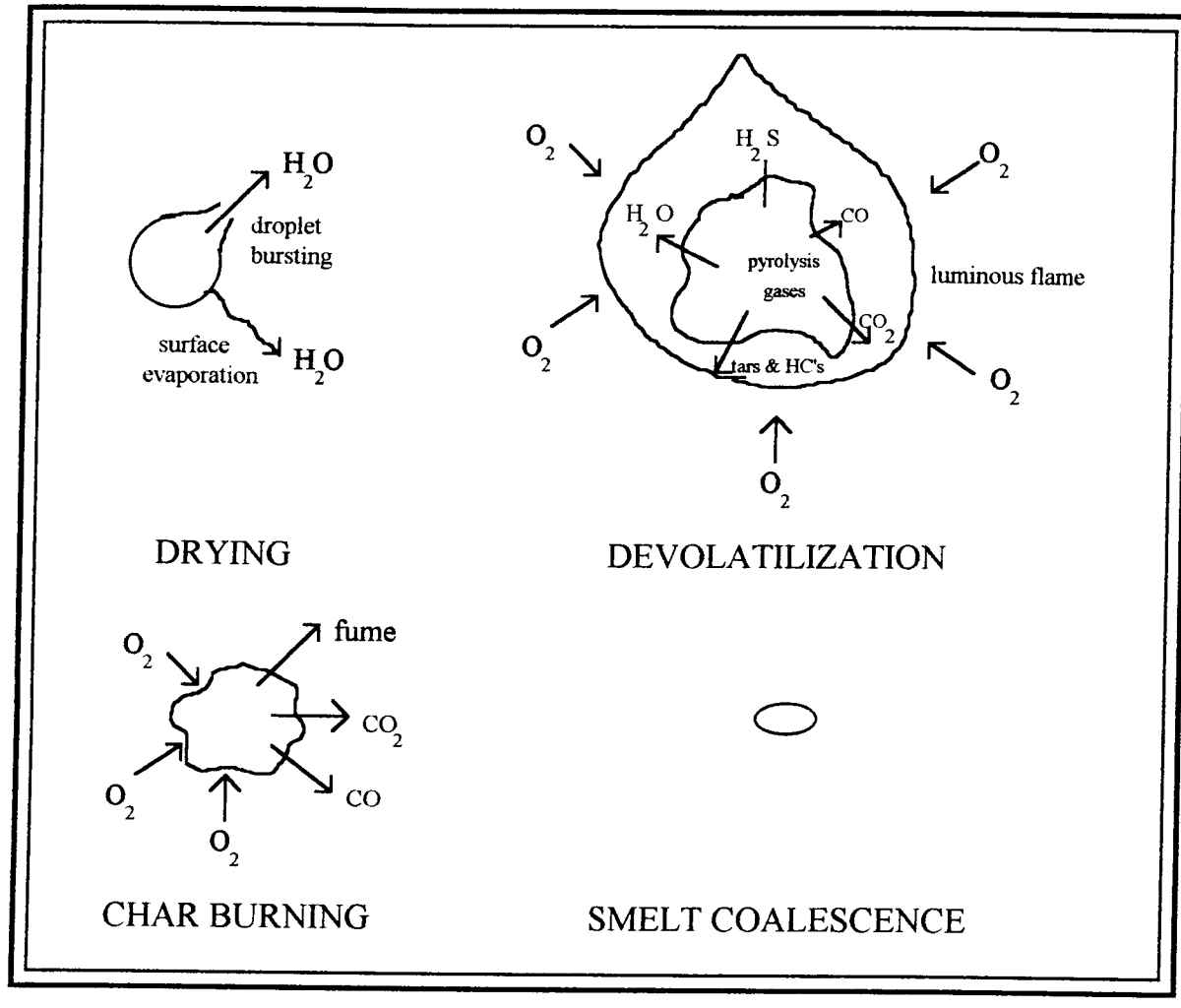


Figure 3.1. Stages in Black Liquor Droplet Combustion
(based on Adams and Frederick, 1988)

Drying begins immediately when the black liquor enters the furnace. Heat is transferred to the particle from the surrounding environment while water is being evaporated from the droplet. The droplet swells slightly in diameter, typically by a factor of 1.5, as water vapor escapes through the particle surface (Frederick *et al.*, 1991; Adams and Frederick, 1988). The drying time is the time interval from when the particle enters the furnace to when the particle ignites, hence "ignition time" (Frederick *et al.*, 1989).

Devolatilization is evident as a yellow flame appears. Devolatilization involves two processes -- pyrolysis and gaseous combustion. Pyrolysis involves the decomposition of the material as a result of rapid particle heating. During pyrolysis, the volatile gases are released. Gaseous combustion results from the combustion of these volatile gases. The black liquor particle swells significantly during devolatilization, usually by a volume factor of 20-50 depending on the liquor type (Frederick *et al.*, 1991). Pyrolysis gases (volatiles) evolve from the particle and gaseous combustion occurs. The devolatilization is a relatively fast process. The devolatilization time is either characterized as the time at which the flame appears until the maximum volume of the particle is reached or as the time when a flame is present (Frederick *et al.*, 1989).

The particle resulting from the devolatilization process is a swollen, porous char particle containing mainly carbon and sodium salts. During char combustion, the carbon burns as oxygen is supplied to the char surface and the particle shrinks in size. Carbon dioxide and water vapor can also oxidize the char carbon to CO, which in turn is burned in the surrounding environment. Char burning does not have any visible flame. Instead the char particle tends to glow as the heterogeneous combustion reactions occur. Furthermore, fume particles appear as a result of sodium volatilization. Char burning time is the time elapsed between the disappearance of the flame and the complete carbon burnout (Frederick *et al.*, 1989).

During char combustion, the temperatures are high enough to melt the sodium based salts in the char particle. Smelt coalescence occurs at the end of char burning when the particle collapses into a smelt bead.

3.2 NO_x Formation in Black Liquor Combustion Processes

Nichols and Lien (1993) have conducted studies to determine the relative importance of fuel NO_x and thermal NO_x formation in black liquor combustion. Their

experiments were done in a drop tube furnace which has a char bed and a gas-particle counterflow. They compared the NO_x levels generated from the combustion of black liquor in air and in 21 % O_2 in argon (Ar) at the same reactor operating conditions. They discovered air leakage during the combustion with synthetic air which resulted to an average of 16% N_2 contaminant. However, there was no apparent change in the measured NO_x levels when the N_2 was reduced from 80 % to 16 %. This indicates that the N_2 in the combustion air has no effects on NO_x formation and that the NO_x was generated from fuel N. They further discussed that reported peak gas temperatures in recovery boilers are not high enough to produce significant amounts of thermal NO_x. Acoustic measurements at 7.5 m from the liquor guns were reported to be 1200°C at design load and 1320°C at higher loading in one recovery boiler (Whitten *et al.*, 1989). Nichols and Lien (1993) showed that in order to have a significant thermal NO_x formation at low temperatures, long enough residence time is needed; *i.e.*, at 2 seconds and 10 % O_2, the temperature required to produce 10 ppm of thermal NO is 1430°C.

Thermal NO formation is sensitive to temperature and moderate increases in furnace temperature (55-80°C) will yield order of magnitude increases in thermal NO formation (Nichols *et al.*, 1993). However, unlike thermal NO, the formation of fuel NO is less sensitive to temperature. Observations by Nichols and co-workers on the NO_x emissions from different recovery furnaces that feed different solids concentration showed moderate increases in NO_x emissions; from 30 ppm to 90 ppm (@ 8% O_2) as solids increased from 65 % to 80 % solids. It was estimated that there is a 230°C temperature increase during black liquor combustion when the solids concentration was increased from 65 to 80% (Adams and Frederick, 1988). If the NO_x formation was due to thermal NO_x, the increase in thermal NO_x emissions should have increased by a factor of several hundred for a 230 °C temperature increase. Nichols and co-workers thus concluded that fuel NO formation was more important than thermal NO formation in recovery boilers. In the studies presented, the prompt NO_x has been considered insignificant since it was

believed that the overall contribution of prompt NO_x formation to the total NO_x emissions is negligible.

Another factor that determines the fuel NO_x emission levels is the amount of nitrogen in the liquor. Nichols and Lien (1993) also conducted experiments on the effect of fuel nitrogen to NO_x formation in the drop tube furnace. Low-nitrogen synthetic black liquor (0.012 wt % N) and mill black liquor (0.087 wt % N) were burned with 21 % O_2 at 1 second residence time and 800°C. At these conditions, thermal NO_x is undetectable. The NO_x levels were 18 ppm and 75 ppm for the synthetic liquor and mill liquor respectively. This shows that the fuel NO_x emissions increase as the liquor nitrogen content increases and that the fractional conversion to NO increases with decreasing nitrogen content. The nitrogen content of kraft black liquors range from 0.04 to 0.26 weight percent (wt %) of dry BLS, with an average of 0.11 wt. %. About 20 % of this amount accounts for the typical levels of NO_x emission in recovery boilers, approximately 25 to 120 ppm (@ 8% O_2) (Nichols *et al.*, 1993).

During black liquor combustion, the concentration of oxygen in the gas also determines the amount of NO formed. If only low concentrations of O_2 are available in the proximity within the furnace where the nitrogen is evolved from the black liquor, less fuel NO_x will be formed (Nichols and Lien, 1993). The availability of O_2 is controlled by the distribution of air in the kraft recovery furnace, *i.e.*, air-staging.

Because fuel NO_x was found to be the major source for NO_x emissions during black liquor combustion, the volatilization of nitrogen in black liquor is currently of interest for NO_x control studies. Perhaps the most important data for black liquor pyrolysis studies so far were presented by Aho *et al.* (1993). The experiments were carried out in a tube furnace where a single droplet of black liquor was suspended in a hook for 300 seconds while Ar was allowed to flow downward past the droplet and to the gas analyzers. The amount of fixed nitrogen, N_{fix} (NH_3 and NO), released during devolatilization was monitored at the temperature range of 300 - 950°C. The main part of

nitrogen evolution took place in the pyrolysis stage rather than the drying stage. They also found that the rate of fixed nitrogen release increases with increasing temperature. A maximum level of N_{fix} occurred at temperatures between 600 - 800°C. At temperatures higher than 800°C, a part of N_{fix} decreased probably due to the formation of molecular nitrogen in the pyrolysis gas stream. The fate of fuel-bound nitrogen is summarized in **Figure** 3.2. The product yield depends on the liquor type. There was about 10 - 30 % NH_3 intermediate formed and only 1 - 2 % of the fuel N was completely converted to NO during pyrolysis. In the study, there was no HCN present indicating either that HCN was not formed in black liquor pyrolysis or that all HCN may have been converted to NH_3. It has been observed that when fuel nitrogen is present in the form of aliphatic amines as may be the case of black liquor droplets, NH_3 becomes the principle product of fuel nitrogen conversion (Houser *et al.*, 1980). This may explain why HCN was not present in the experiments of Aho *et. al.* (1993).

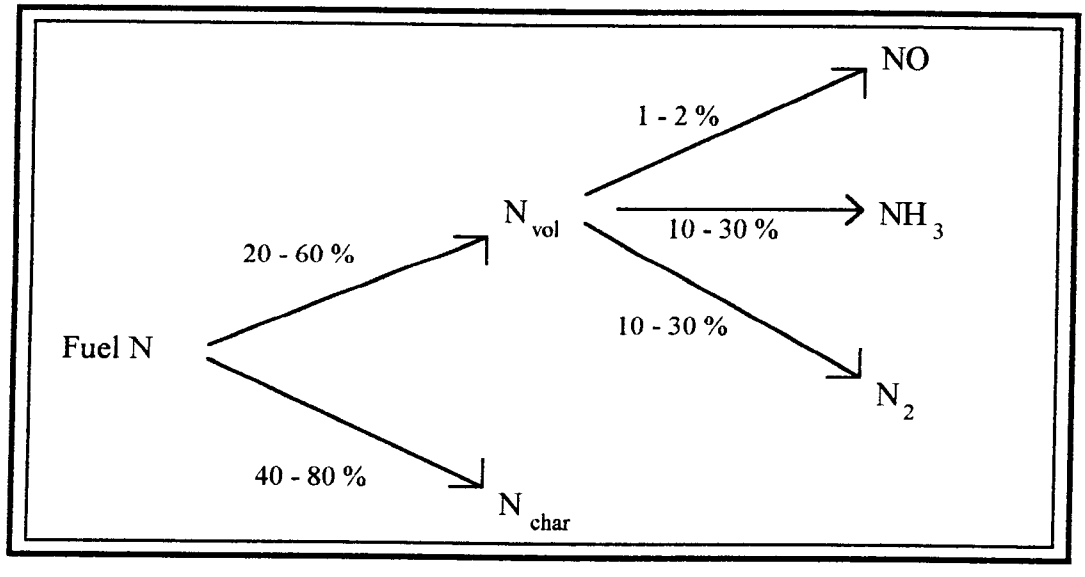


Figure 3.2. Behavior of Fuel Nitrogen During Black Liquor Pyrolysis
(based on Aho *et al.*, 1993)

The effective yield of NO_x in the pyrolysis experiments by Aho *et. al.* (1993), assuming that all NH_3 is converted to NO, accounts for the typical NO_x emission levels in kraft recovery furnaces. This shows evidence that a significant part of fuel nitrogen responsible for NO_x formation may be released during the pyrolysis stage.

Nichols and Lien (1993) concluded in their study that substantial amount of nitrogen release and NO_x formation occurred during devolatilization. In the drop tube furnace consisting of a char bed and a particle-gas counterflow, 40 % of the maximum NO_x was produced near the char bed. The NO_x content of the gases increased with increasing distance from the char bed surface where the remaining 60 % of the NO_x was formed during in-flight combustion. However, there was an apparent decrease in NO at distance farthest from the char bed. It was assumed that NO_x may have reacted with other gas species.

Nichols and Lien (1993) also conducted devolatilization tests in which mill liquor solids in closed crucibles were heated at 700°C in a muffle furnace. In the liquor studied, nitrogen evolved at a rate slightly higher than the carbon evolution rate. At the completion of pyrolysis, approximately 50 % of the fuel nitrogen had volatilized. This further supports their conclusions that nitrogen evolution and consequently NO_x formation occurs during devolatilization.

3.3 NO_x Depletion and Reduction Mechanisms in Black Liquor Combustion

NO can also be reduced during combustion. As in fossil fuel combustion, NO_x decay in black liquor combustion can be attributed to homogeneous gas phase reactions and heterogeneous reactions with char. Furthermore, with significant amounts of alkali species present in black liquor combustion, NO_x depletion by reaction with sodium species has been proposed at the Institute of Paper Science and Technology and at Oregon State University.

Reversible Zeldovich Mechanism

Under the right conditions, the reverse reactions for the Zeldovich mechanism may contribute to the depletion of NO (Thompson and Empie, 1993). However, these reactions are only favored at high NO concentrations and suffer the same temperature sensitivity as the forward reactions. Kinetic modeling by Klinger *et al.* (1984) has shown that these reactions are only important at temperatures above 1477°C. Therefore, NO depletion by thermal decomposition should not have significant effects on NO_x emissions from recovery furnaces.

Homogeneous reactions with other gas phase species

In **Figure** 2.1 in **Chapter** 2, NO can form N_2 by reacting with NH_i species or NO itself. The process consists of a chain branching mechanism initiated by the reaction of NH_i with NO. At high temperatures (above 1500 K), the process is counterproductive as it promotes NO formation; at low temperatures (below 1000 K), the reaction is inhibited as the chain termination steps dominate the chain branching steps (Miller *et al.*, 1981).

The gas phase decomposition of NO by combustion gases -- H_2, CH_4, C_2H_6, CO and NH_i -- has been studied and reported (Muzio *et al.*, 1976). The NO-reducing agents were added to primary combustion products downstream of the main combustion zone. They found that only minor NO reduction was achieved at ratios of CO/NO or H_2/NO up to 14 since these species, as well as CH_4 and C_2H_6, rapidly react with excess oxygen in the combustion products. However, 78 % NO reduction was achieved at an optimum temperature of 1240 K and 1:1 molar ratio of NH_3 to NO. This has been the basis of postcombustion control strategies as will be shown in **Section 3.4**.

Heterogeneous reactions with char

It has been observed that NO reduction may be attributed, in part, to heterogeneous reactions with char. This arises from the fact that the rate of NO reduction in coal flames was observed to be much higher than that in the combustion products of gases and liquids. Levy *et al.* (1981) proposed a mechanism responsible for the NO/char reaction and it is as follows

$$NO + 2C \Rightarrow C(N) + C(O) \quad (3.1)$$

$$C(N) + C(N) \Rightarrow N_2 + 2C \quad (3.2)$$

where C represents a surface carbon, C(N) and C(O) are chemisorbed nitrogen and oxygen atoms. The chemisorbed oxygen can either be desorbed to produce CO or react with CO to produce CO_2

$$C(O) \Rightarrow CO \quad (3.3)$$

$$C(O) + CO \Rightarrow CO_2 + C \quad (3.4)$$

The NO/char reaction is slightly inhibited by the presence of water vapor and slightly enhanced by CO. This enhancement of CO decreases with increasing temperature.

Wu (1994) recently completed his study on NO and black liquor char reactions. He found that the rate of the NO/char reaction per gram of char , r_{NO}, is given by

$$r_{NO} = 21.58 \exp\left(\frac{-67.3 \text{ kJ}}{RT}\right) S_a C_{NO} \qquad \frac{\text{moles}}{\text{g sec}} \quad (3.5)$$

where S_a is the internal surface area of the char in cm^2/g, and C_{NO} is the concentration of NO in $moles/cm^3$. The rate of NO reduction is shown to be dependent on the surface area of the char, the NO concentration, temperature and residence time.

The impact of NO/char reactions in black liquor combustion is currently unknown. In recovery boilers, there are large char particles in flight and the impact of NO/char reactions may be significant. The sodium salts in the black liquor char were shown to

increase the NO reduction rate by orders of magnitude compared to other carbonaceous compounds (Wu, 1994).

NO_x reactions with fume

Although it was ignored in fossil fuel combustion, the impact of sodium species on NO reduction could be significant in recovery boilers. The fume resulting from black liquor combustion is primarily composed of sodium compounds. Thermodynamically, sodium nitrate ($NaNO_3$) formation reactions are feasible at temperatures found in the upper furnace (Thompson and Empie, 1993). However, the catalytic reduction of NO by sodium species is also possible. These catalytic reactions during black liquor combustion are currently being investigated at Oregon State University.

NO_x reactions with molten salts

Molten salts are found in the char bed as well as in black liquor droplets that have reached the final stages of combustion (char burning and smelt coalescence) while in flight. Thompson and Empie (1993) proposed that the reactions of NO_x with the molten salts are similar to the reactions involved with fume except that they occur at higher temperatures and with different surrounding gases. The authors have analyzed smelt samples from several kraft recovery mills for nitrates (NO_3^-) and found nitrate levels ranging from 1590 to 10,780 ppm. However, the accuracy and importance of this finding have not been verified.

3.4 Effectiveness of Traditional NO_x Emission Control in Kraft Recovery Boilers

Some of the common techniques in NO_x control make use of the NO_x depletion mechanisms presented in the previous section. The NO_x emission control techniques include the selective catalytic reduction process, the selective non-catalytic reduction process, flue gas recirculation, and air-staging. These techniques are currently being enforced by the Clean Air Act Amendments of 1990.

Selective Catalytic Reduction Process (SCR)

This involves ammonia injection in the flue gas whereupon an intimate mixing with NO_x occurs. The resulting gas mixture then passes through a catalyst bed that selectively promotes the reduction of NO to N_2. The major components of the catalyst are titanium dioxide (TiO_2), vanadium pentoxide (V_2O_5), and molybdenum trioxide (MoO_3); the respective composition varies depending on manufacturers (Cho, 1994). The catalyst effectively lowers the activation energy of the NO decomposition reaction. The dominant reaction that occurs in a SCR is given by

$$4\,NO + 4\,NH_3 + O_2 \Rightarrow 4\,N_2 + 6\,H_2O \qquad (3.6)$$

Low temperatures of 533 - 727 K are required for longer catalyst life and prevention of NH_3 oxidation to NO (Anderson and Jackson, 1991). The NO_x removal efficiencies of the SCR range from 42 % to 90 % (Cho, 1994).

Maximum reduction can be achieved when excess ammonia is injected (Hampartsoumian and Gibbs, 1982). The quantity of excess ammonia exiting the process is also known as ammonia slip. The NO_x removal efficiency increases with increasing inlet ammonia concentration. However, it reaches an asymptotic value at a certain level of excess ammonia thus indicating that there is a limit to the advantageous effect of excess ammonia in NO_x removal (Cho, 1994). Anderson and Jackson (1991) explained that the sulfuric acid (H_2SO_4) and hydrochloric acid (HCl) present in furnace exhaust stream can

react with excess ammonia to form ammonium salts -- ammonium sulfate [$(NH_4)_2SO_4$], ammonium bisulfate (NH_4HSO_4), and ammonium chloride (NH_4Cl). The ammonium sulfate and ammonium bisulfate can foul low temperature heat exchange equipment below standards of protection. The ammonium chloride, which is formed at low temperatures, is released at the stack outlet and into the atmosphere as a visible plume that could exceed opacity standards. Any ammonia that does not react in the flue gas is environmentally harmful when released in the atmosphere.

Selective Non-Catalytic Reduction Process (SNCR)

The method makes use of a reducing reagent such as ammonia or urea [$CO(NH_2)_2$] for the homogeneous decomposition of NO_x to N_2 and H_2O. The NO_x removal efficiencies of the SNCR range from 25 % to 50 % (Wood, 1994).

The SCNR system is only effective at a specified temperature range, usually 1144 - 1177 K. Anderson and Jackson (1991) argued that although the temperatures exist in the recovery furnace, maintaining the optimum reaction temperature at sufficient reaction time may not be possible. Furthermore, the effects of reagent injection on important recovery furnace processes of smelt reduction and black liquor combustion have not been investigated.

This method suffers the same detrimental effects of excess ammonia as the SCR system. Anderson and Jackson (1991) argued that the reagent slip problem is complicated because it is influenced by interrelated factors such as flue gas concentrations, residence time, reagent and flue gas mixing, and type of heat recovery equipment used. Furthermore, maintaining the proper reagent/NO_x molar ratios is difficult due to fluctuating furnace operations, flue gas temperatures and NO_x emission rates. Other problems include corrosion and fouling of heat transfer equipment.

Flue Gas Recirculation (FGR)

The method involves extracting a portion of flue gas and returning it to the furnace to reduce the peak flame temperature and the oxygen available for NO formation. The flue gas can be recirculated after the electrostatic precipitator to prevent high dust loadings. Additional tests are needed to determine operating conditions needed to achieve optimum NO reduction.

Air-Staged Combustion

The principle of air staging is primarily to reduce the level of available oxygen in zones where it is critical for NO_x formation. The peak flame temperature is also reduced. The air can be staged in the furnace or in the burner, *i.e.*, low-NO_x burners, although a mixture of both is commonly used.

Air staging in the furnace produces two stages -- primary and secondary. In the primary stage, the fuel is burned at an air/fuel stoichiometric ratio that gives the minimum total fixed nitrogen species. The secondary air is injected downstream from the primary stage to provide for burnout of CO and hydrocarbons in the primary stage products. The second stage usually requires excess air and thus, a significant fraction of the fixed nitrogen species is converted to NO_x. Generally 10 - 20 % of the total combustion air is used for the second stage, but 20 - 30 % is being considered for further NO_x reduction (Bowman, 1991). The NO_x reduction achieved by air staging in the furnace ranges from 30-60 % (Wood, 1994).

Air staging in the burner achieves the staging effect internally. The air and fuel flow fields are partitioned and controlled to achieve the desired air/fuel ratio that reduces NO_x formation and results in complete burnout. Low-NO_x burners achieve 30-50 % NO_x reduction (Wood, 1994).

Air-staging is a built-in feature of the kraft recovery furnace. **Figure** 1.2 in **Chapter 1** shows three stages in which air is added. The difficulties of staged combustion in recovery boilers arise due to the complexity of flow patterns and mixing of fuel (Someshwar, 1992). The flow patterns for each furnace are somewhat unique. Several tests are required to achieve optimal operating conditions.

CHAPTER 4
EXPERIMENTAL METHODS

4.1 Experimental Set-up

The experimental set-up is shown in **Figure** 4.1. The different parts are as follows

- Laminar Entrained Flow Reactor (LEFR)
- Fourier Transform Infrared Spectrometer (FTIR)
- Chemiluminescence NO-NO_x Analyzer (NO-NO_x meter)
- CO Gas Analyzer
- CO_2 Gas Analyzer
- NH_3 and H_2S absorption bottles
- cyclone/filter assembly

The set-up is used for three simultaneous projects. Besides this study, the fate of carbon, sulfur, sodium, potassium and chloride during black liquor pyrolysis are also being investigated. For the purpose of this study, the relevant equipments include the LEFR, NO-NO_x meter, cyclone/filter assembly, and the NH_3 absorption bottle.

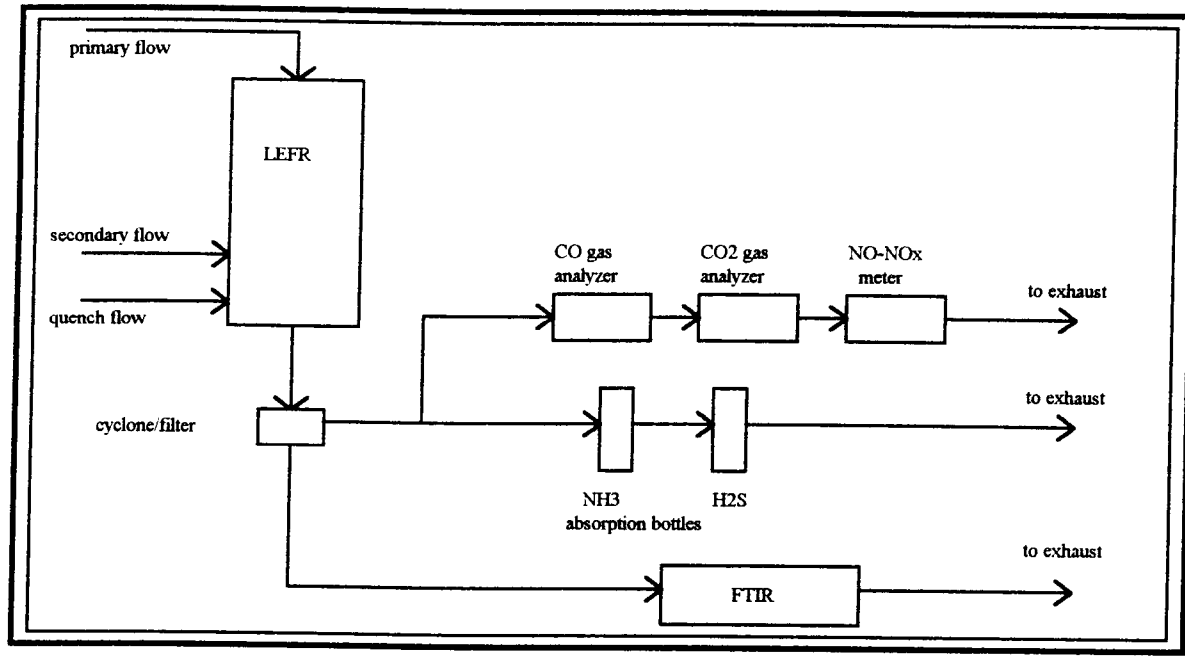


Figure 4.1. Experimental Set-up for the Black Liquor Pyrolysis Experiments

Laminar Entrained Flow Reactor (LEFR)

The LEFR was designed and built by Scott Sinquefield, a Chemical Engineering graduate student at Oregon State University. The operational design is shown in **Figure** 4.2. The LEFR consists of two parts, the reactor and the collector. The reactor is a cylindrical ceramic tube made of mullite with an inside diameter of 70 cm. The reactor is inserted in a tube furnace that is subdivided into three 12 inch furnace zones, each controlled with an Omega CN76000 Microprocessor Based Temperature and Process Controller capable of ramping to its set point temperature at a maximum heating rate of 300 °C/hour. Gas flows into the reactor include primary flow (ν_{pr}) and secondary flow, the sum of which is designated as the total gas flow (ν_{tr}). The quench flow (ν_{qr}) enters through the collector. Currently six Omega FMA5600 Electronic Mass Flow Meters (MFM) are connected to the LEFR to regulate these flows, four (MFMs #1 - #4) of which control the total gas flow to allow a mixture of four gases. The total gas flow is split to

the primary flow and the secondary flow by means of a metering valve. The primary flow is controlled by MFM #5. The quench flow passes through MFM #6 and is split to two rotameters -- one to regulate the flow at the tip of the collector and the other to regulate the flow through the porous wall of the collector body.

The black liquor solids are entrained in and carried by the primary flow from the particle feeder to the injector and into the reactor (refer to the LEFR Operation Manual by Scott Sinquefield for feeder description). Cooling water flows through the injector to prevent any premature heating of the gas and the particles. The secondary flow, on the other hand, enters the LEFR through the bottom, is heated to the furnace temperature as it flows through the outer annulus of the reactor and enters into the reactor through a flow straightener located at the top. The flow straightener occupies the first 3.5 inch of the reactor space and is used to enforce uniform secondary gas flow. Lastly, the quench flow enters the collector to cool down the gases passing through it.

The collector can be moved inside the reactor to vary the reactor pathlength. The effective length of the reactor ranges from 4 inches to 30 inches. Equivalent residence time ranges from 0.5 seconds to 4.5 seconds depending on the furnace temperature and the gas flows employed. The outer part of the collector consists of a layer of ceramic insulation and a two-pass shell for cooling water to prevent the heating of the quench gas. The inner wall of the collector is porous to allow the distribution of quench gas flow. The larger pores at or near the tip of the collector, have one primary function -- to allow a rapid decrease of the reactor gas temperature. The smaller pores throughout the collector body have two functions -- to further decrease the temperature of the reactor gas and to prevent particles from depositing to the walls of the collector.

The reactor effluent and the quench gas flow into the cyclone, and particles greater than 5μm in size (char) are collected. Then the flow is filtered to obtain fume particles by means of three filters -- two 0.47 cm filters (filter 1 and filter 2) with 0.22 μm pore size before it flows to the gas analyzers and one 9.0 cm filter (filter 3) with 0.8 μm pore size --

before it exits to the exhaust. Refer to **Figure** 4.3 for an illustration of the cyclone/filter assembly. Nylon membranes are recommended if fume analysis is desired; however, quartz filters, which can react with sodium salts, are sufficient if only the fume weight is needed.

The LEFR operates at standard atmospheric pressure. To enable the flows into the analytical instruments, pumps are required downstream. The NO-NO_x meter has its own pump that pulls the gas samples from the LEFR to the CO and CO_2 gas analyzers and into the meter's reaction chamber for NO analysis. The FTIR gas cell is initially under vacuum, enabling gases to flow freely into the cell. The absorption bottles, however, require an external pump to pull gases from the LEFR. The pump is placed downstream from the absorption bottles and a mass flow meter, MFM #7. MFM #7 regulates the flow being pulled by the pump.

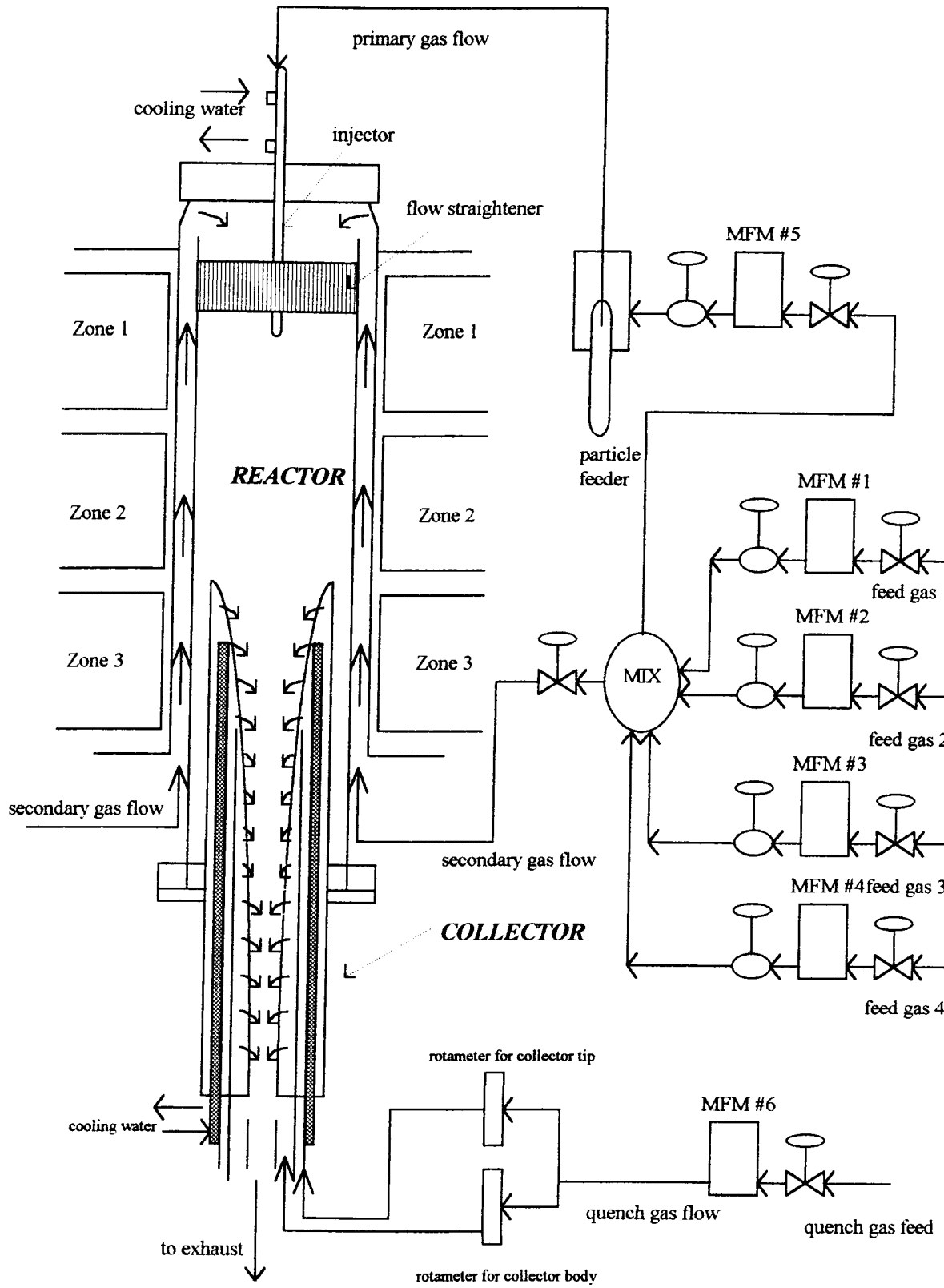


Figure 4.2. The Laminar Entrained Flow Reactor

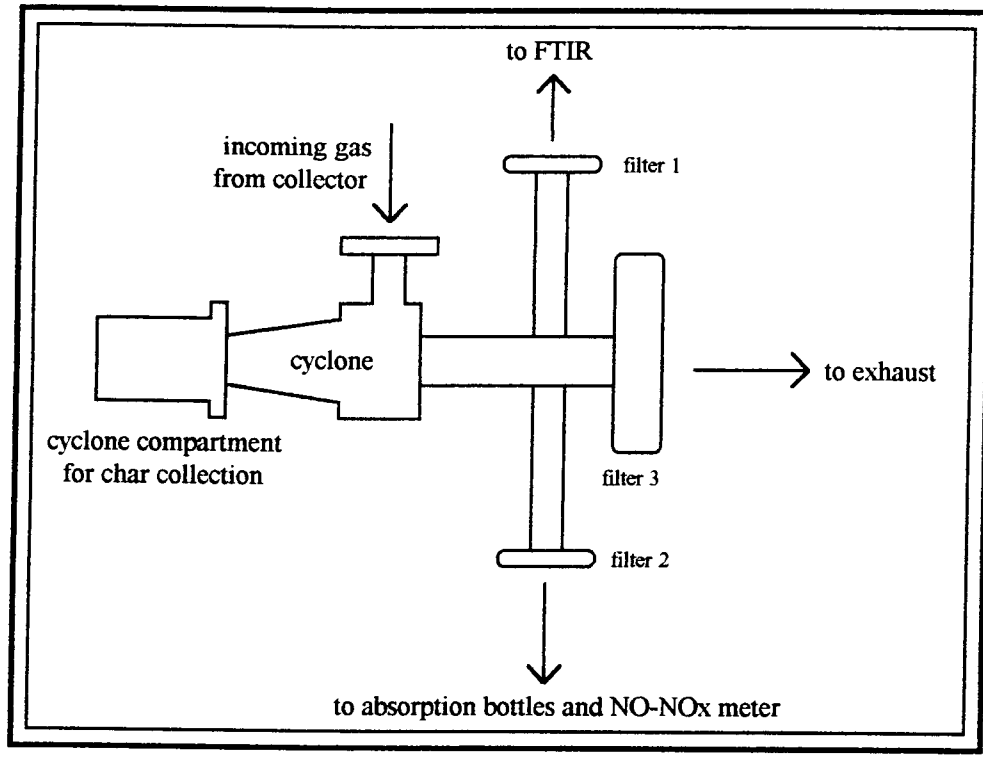


Figure 4.3. Cyclone/Filter Assembly

Chemiluminescence NO-NO_x Gas Analyzer (NO-NO_x meter)

The meter is a Model 10AR NO-NO_x gas analyzer manufactured by Thermo Environmental Instruments Inc. It is capable of continuous measurements of NO-NO_x with 8 linear full-scale ranges from 2.5 to 10000 ppm. The instrument is equipped with a reaction chamber for the chemiluminescence reaction of NO and O_3 molecules

$$NO + O_3 \Rightarrow NO_2 + O_2 + h\upsilon$$

The resulting light emission is monitored through an optical filter by a high-sensitivity photomultiplier. The output from the photomultiplier is linearly proportional to the NO concentration. For NO_x measurements, the sample gas flow enters a NO_2-to-NO converter prior to the reaction chamber. However, for this study, NO_x was not measured

because it was expected that the amount of NO_2 released during the experiments was insignificant relative to NO.

4.2 Experimental Procedure

The gas flows were set based on the desired residence time and the operating furnace temperatures. The equations used in determining the flows are included in **Section** D.2 in **Appendix D**. Prior to the experiment, the flows were adjusted according to the preliminary calculations made. In setting the flows, it was important to turn on the quench flow followed by the total gas flow because the collector body cannot withstand temperatures higher than 800°C. The pressure into MFM #5 was set at 25 psi before opening the primary flow. After adjusting the flows, the shut valves for all MFMs were closed as other preparations were being made.

The range for the NO-NO_x meter was set depending on the gas flows used. The recommended ranges were 0-25 ppm for $\nu_{tr} < 15$ liters/min and 0-10 for $\nu_{tr} > 15$ liters/min. The flow into the NO-NO_x meter was adjusted to have a bypass flow rate of 1.75 scfh (as indicated on the bypass rotameter).

Black liquor particles were weighed and loaded into a test tube. The test tube was inserted in the particle feeder. All gas flows were then fed into the LEFR. The motor for the particle feeder was turned on allowing black liquor solids to be entrained by the primary gas flow. The motor speed was set to low for slower black liquor mass flow rate and longer running time. Immediately after particles started exiting the reactor, the motor for the particle feeder was turned off. However, all gases were left flowing into the reactor and the collector.

The cyclone/filter assembly was then attached to the bottom of the collector and all lines leading to the required analytical equipments were attached to it. The line to the absorption bottle containing 150 ml HCl solution was heated to prevent NH_3 absorption in

the lines. The flow into the absorption bottles, also called the scrubber flow (v_{sr}), was set to about 4 liters/min to obtain measurable NH_3. A FTIR reference gas reading for the study of carbon evolution was taken at this point.

Each run started by simultaneously turning on the motor for the particle feeder and the data acquisition program. The data acquisition program recorded all gas flow rates from the mass flow meters and NO-NO_x meter readings. During the experiment, the reactor effluent was cooled down by the quench gas and upon passing through the cyclone set-up, the char and fume were collected. Ammonia was absorbed in the HCl solution throughout the experiment. Continuous measurements of NO were recorded by the data acquisition program. Instantaneous FTIR readings were taken after 2 minutes of runtime.

At the end of the experiment, the primary flow was turned off and the motor for the particle feeder was placed on the reverse mode (thus, lowering the test tube). These two steps were done simultaneously. The total gas flow and the quench flow was kept flowing into the reactor until the NO level, as displayed in the NO-NO_x meter, was down to zero. The data acquisition program was disabled after all pertinent NO data were gathered. Then all gas flows were shut off. The shut-down procedure assured that the total amount of NO released can be obtained from the data recorded in the data acquisition file.

The fume and char samples were weighed and stored. The cyclone was again assembled and attached to the collector. The particle feed lines were then flushed at the maximum primary gas flow rate for at least 1 minute to clear the lines of any black liquor particles that may have accumulated on the walls of the feed system. The char and fume collected from this step were weighed but not stored.

As a final procedure, the NO calibration gas was allowed to pass through the NO-NO_x meter and readings were recorded into the same data acquisition file as the experiment. This provided current NO calibration for the experiment.

Preparations for the next run required back-flushing that ultimately cleans the injector of black liquor particles. In this procedure, the stainless steel tube attached to the injector was removed. The quench gas was turned on to at least 25 liters/min. The collector outlet was plugged by a piece of metal for at least 20 seconds. This reverses the flow of the quench gas, which exits through the injector and cleans it of any remaining particles.

Appendix B contains the experimental guidelines used in the experiment.

4.3 Analytical Instrumentation and Procedures

The main compounds that were of interest in this study were NO, NH_3, and the nitrogen retained in the char (char-N). **Table** 4.1 shows the particular instruments used for analysis.

Table 4.1. Method For Analysis

Method/Instrument	Compound/s Analyzed
Chemiluminescence NO-NO_x meter	NO
Ion-Selective Electrode	NH_3 absorbed in 0.01 M HCl solution
Kjeldahl Analysis	char-N

Ion-Selective Electrode

The ammonia electrode is a Model 95-12 Orion ion-selective electrode (ISE). It was used to measure the total amount of ammonia absorbed in the HCl solution. It was also used to measure ammonia in fume, but none was detected. Ammonia was measured in the units of ppm NH_3 in solution. Amines were the only compounds known to interfere

with the readings. Refer to **Appendix C.1** for detailed procedures in the operation and analysis using the ISE.

Kjeldahl Analysis

The analysis was performed by the team of Dr. Dean Hanson from the Oregon State University Plant Analysis Lab in the Department of Soil Science. About 0.4 grams of the char was weighed and sent for duplicate analysis of total nitrogen concentration. It was necessary to have duplicate analysis because the total nitrogen concentration was estimated to be at or near the detection limit. The error in the analysis is ± 0.01 wt. % N.

The Kjeldahl analysis involved two processes: (a) digestion of the sample and (b) determination of NH_4^+ in the digest. The char sample was subjected to high-temperature digestion from 150 to 350°C with concentrated H_2SO_4 and catalysts to convert forms of N to NH_4^+. The sample was then distilled and the NH_3 distillate was trapped in boric acid solution for further titration with H_2SO_4 . The amount of H^+ needed for titration was equivalent to the amount of NH_4^+ in the digest.

Data Acquisition Program

The Omega WB-ASC Card produced by the Omega Engineering, Inc. was used for data logging. The data acquisition program recorded the time-averaged readings from the mass flow meters and the NO-NO_x meter (CO and CO_2 readings are also recorded) during the experiments. Data were acquired every 2 seconds. NO levels were determined either by using the average concentration at steady state or by obtaining the total NO detected by the NO-NO_x meter for each run. Refer to **Appendix C.2** for equations used regarding the data file analysis.

4.4 Materials

This study involved only one black liquor -- a southern pine liquor -- obtained from a kraft pulp mill in Georgia. The black liquor solids (BLS) were obtained by drying and grinding of the dry solids to fine particle sizes. The particle size range used was 90-125 μm. The total nitrogen analyses for five samples of the same BLS was performed at the Oregon State University Plant Analysis Lab in the Department of Soil Science. The reported values for the five samples were 0.126, 0.118, 0.105, 0.108 and 0.097 % by weight. The average nitrogen content of 0.111 wt. % was used for calculations. The analysis of the BLS is presented in **Table** 4.2.

Table 4.2. Analysis of the Black Liquor Solids

Element	wt.% BLS
carbon (C)[a]	35.7 %
hydrogen (H)[b]	3.05 %
nitrogen (N)[c]	0.111 %
sodium (Na)[b]	22.65 %
potassium (K)[b]	0.619 %
sulfur (S)[a]	2.85 %
chloride (Cl)[b]	0.672 %
oxygen (O)[d]	34.35 %

a new sample analysis made by Weyerhaeuser Co. in summer '94
b old sample analysis made by Weyerhaeuser Co. in spring '93
c new sample analysis by the team of Dr. Dean Hanson in summer '94
d obtained by difference

4.5 Operating Conditions

Preliminary experiments were made in the LEFR to determine the feasibility of the experimental and analytical methods. An injector having an inside diameter of 3.34 mm was used for these experiments. With this injector, a primary gas flow rate sufficient to entrain particles in the feeder resulted in a ratio of primary to secondary gas velocities of 3.27 to 3.64. This made it difficult to estimate the residence time in the reactor. The black liquor solids were pyrolyzed at temperatures of 700, 800, 900, 1000 and 1100°C. The reactor pathlength was 17 inches. The gas flows were kept constant at v_{pr} = 0.1 liters/min, v_{tr} = 13 liters/min, and v_{qr} = 20 liters/min. The feed gas used was N_2.

The major part of this study used an injector with a larger inside diameter -- 6.52 mm. With this newer injector, the primary and secondary gas velocities were the same and more accurate estimates of residence times were obtained. **Table** 4.3 shows the operating conditions used in examining the effects of temperature and residence time on fuel NO formation during black liquor pyrolysis. The pathlength was varied from 7 to 30 inches. The feed gas was N_2 and the gas flows were calculated based on the equations presented in **Appendix D**. Runs were made in duplicates or triplicates at each operating condition. This was necessary to verify that the results were reproducible, given the fact that the black liquor particles had the tendency to accumulate in the injector.

Table 4.3. Matrix For Operating Conditions

residence time (seconds)	Temperature (°C)					
	600	700	800	900	1000	1100
0.5			x	x		
0.75		x	x	x		
1		x	x	x		
1.25		x	x	x		
1.5		x	x	x		
1.75		x	x	x		
2	x	x	x	x	x	x
2.25		x	x	x		
2.5		x	x	x		
2.75		x	x			
3				x		
3.25		x	x			
3.5		x	x			
3.75				x		
4		x	x			

CHAPTER 5
EXPERIMENTAL AND ANALYTICAL RESULTS

5.1 Feasibility Studies in the LEFR

Preliminary experiments were made using the old injector (d_i = 3.34 mm) and the new injector (d_i = 6.52 mm). The results are presented in **Appendix E**. The following conclusions were derived from these preliminary experiments:

- The new injector was required to maintain equal total gas and primary gas velocities ($u_p = u_t$). The residence time was estimated more accurately when $u_p = u_t$.
- About 3 to 30 %, with an average of 27 %, of the black liquor feed (BL_{feed}) accumulated in the new injector during an experiment. Thus, it was necessary to collect additional char and fume particles from the feed system during the flushing routine. These additional particulates were considered to be products of the black liquor particles that accumulated in the injector during the actual experiment. **Eqns.** A.3 and A.4 in **Appendix A** estimated the char yield (γ) and the amount of actual black liquor fed into the reactor (BL_{actual}) by taking into account the particulates collected during the experiment and the flushing routine. The char yield is defined as the fraction of black liquor feed that became char.
- The NO released could be estimated by obtaining either the average NO (NO_{mean}) or the total NO (NO_{total}). The NO_{mean} and the NO_{total} were calculated based on **eqns.** C.2.3 and C.2.4 in **Appendix C**, respectively. However, it was found that NO_{mean} tends to overestimate the NO by as much as 60% of NO_{total}. Refer to the summarized results tabulated in **Appendix D**. The lack of a true steady state made it difficult to determine the time interval at which the NO levels could be averaged. In most of the experiments, a steady state was not even apparent. It was then concluded that NO_{total} was appropriate in analyzing NO levels.

- The NH_3 was found to be difficult to analyze because it adsorbs readily onto the surfaces. The absorption bottle technique seemed to work well when a known concentration of NH_3 gas (about 1 ppm) was allowed to pass directly through the absorption bottle. The error was roughly $\pm 20\%$. However, during the experiments, the NH_3 results were irreproducible. The ammonia absorption technique was kept the same in all the experiments. Furthermore, duplicate ISE readings taken on the same sample solutions showed reproducibility. Nevertheless, the data obtained were so scattered that no conclusive information was obtained. Refer to **Figure** E.7 in **Appendix E**. A co-worker tested the effects of passing NH_3 into the LEFR before it was absorbed in the absorption bottles. It was found that most of the NH_3 was lost (Pianpucktr, 1994). It was believed to have adsorbed somewhere in the LEFR. This might have been the reason why the results for NH_3 were not reproducible.
- The results for those experiments with black liquor mass flow rates less than 0.3 g/min should be disregarded because significant mass loss in the feed system may have occurred.

The succeeding experiments were done based on these preliminary conclusions. The NH_3 in the reactor effluent was still collected using the absorption technique for some of the experiments to examine any noticeable trends.

5.2 Effects of Temperature on Nitrogen Evolution

Black liquor pyrolysis experiments were made at furnace temperatures 600 - 1100 °C and a constant residence time of 2 (± 0.1) seconds. The data (except for NO formation) was also obtained at 500 °C. The raw data taken during the experiments are included in **Table** A.2 in **Appendix A** and the analytical results are in **Table** D.2 in **Appendix D**.

Figure 5.1 shows the amount of fuel N that was converted to NO. A maximum in NO formation was observed at 800 °C. Depending on the temperature, near zero to 20 % of the fuel N was converted to NO. The amount of fuel N that was converted to NH_3 is shown in **Figure** 5.2. Similar to the preliminary results, the data points are so scattered making the results on NH_3 formation inconclusive. It was, however, observed that a minimum range of near zero to 6 % of fuel N formed NH_3. This range was considered the minimum because some of the NH_3 may have been lost in the LEFR or in the lines.

The char yield is plotted in **Figure** 5.3. The char yield was based on the char collected during the experiment ($char_{ex}$) and the black liquor particles that were actually fed into the reactor (BL_{actual}). The char yield and BL_{actual} were calculated based on **eqns.** A.2 and A.4. The char yield decreased with increasing temperature.

The total nitrogen analyses of the char are presented in **Table** A.7 in **Appendix A**. The total nitrogen analysis was run in duplicates. Some of these duplicate analyses differed by more than 0.01 wt. %. The average nitrogen content for each experiment is plotted in **Figure** 5.4. The weight of nitrogen retained in the char relative to the weight of the char could be assumed constant with temperature. The average nitrogen content in the char was calculated to be 0.10 wt. %. The standard deviation was 0.01.

Figure 5.5 shows the fuel N that remained in the char (char-N) after pyrolysis. The char-N ranged from 35 - 65 % of the fuel N depending on the furnace temperature. The amount of char-N was found to be decreasing significantly with temperature.

Figure 5.6 shows a bar graph that accounts for the percentage of fuel N that was converted to NO and that remained in the char. The data points plotted in **Figure** 5.6 are averaged values for the duplicate (or triplicate) experiments done at each furnace temperature. Due to the uncertainty in the data, the conversion of fuel N to NH_3 is not shown. From **Figure** 5.6, it can be observed that the sum of NO and char-N seemed to be constant between 600 - 800 °C. At higher temperatures, the sum of NO and char-N decreased significantly.

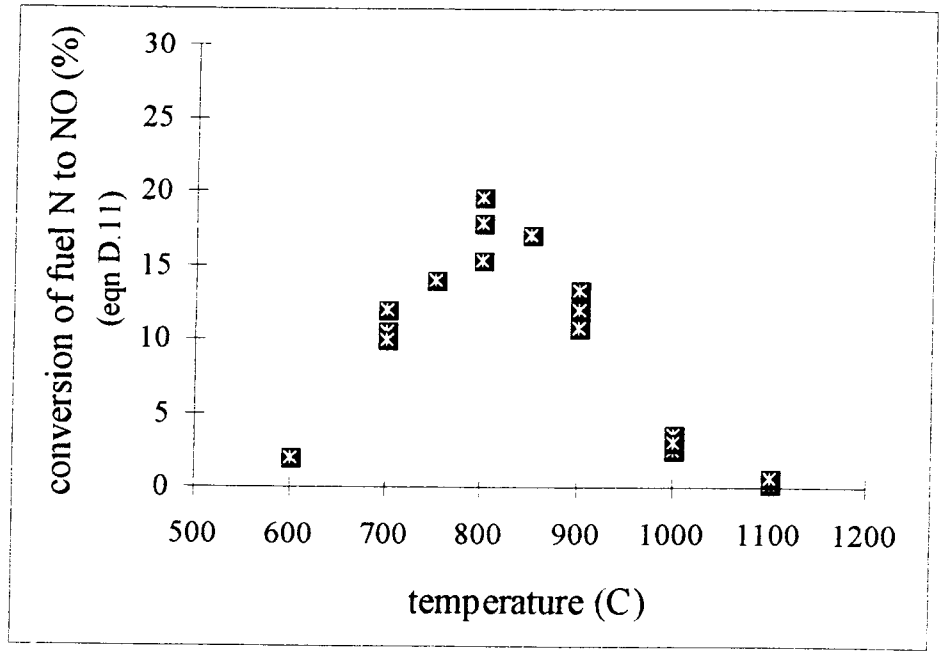


Figure 5.1. NO Formation as a Function of Temperature
(residence time = 2 seconds)

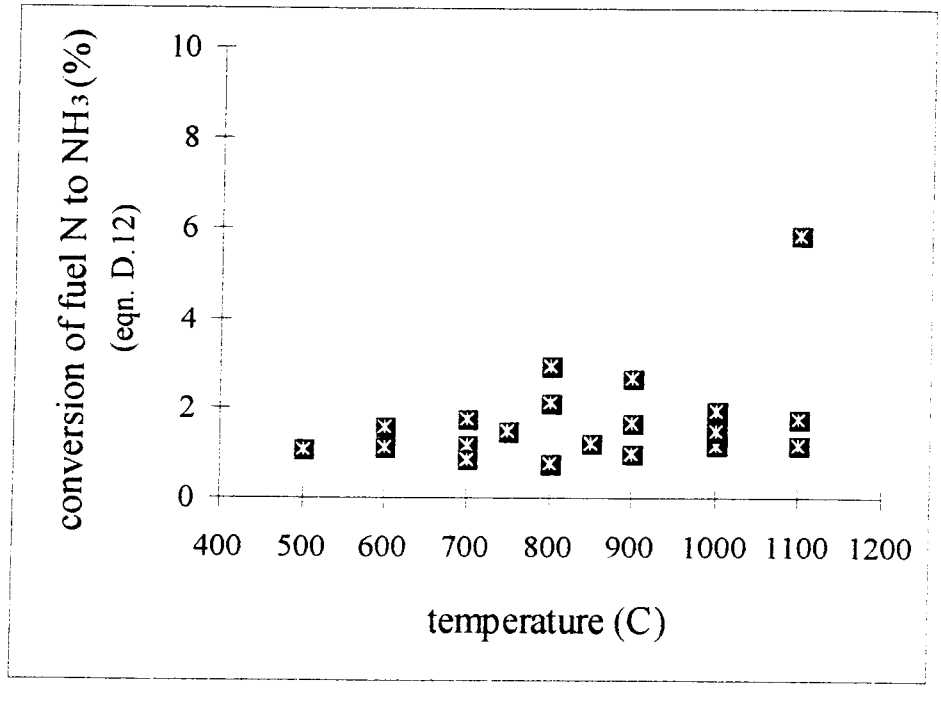


Figure 5.2. NH_3 Formation as a Function of Temperature
(residence time = 2 seconds)

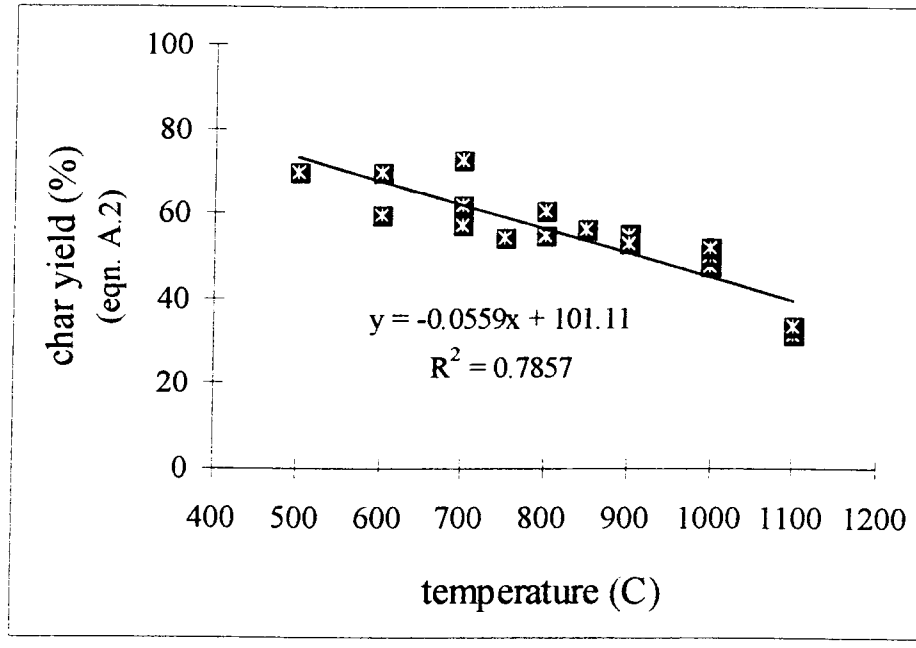


Figure 5.3. Char Yield as a Function of Temperature
(residence time = 2 seconds)

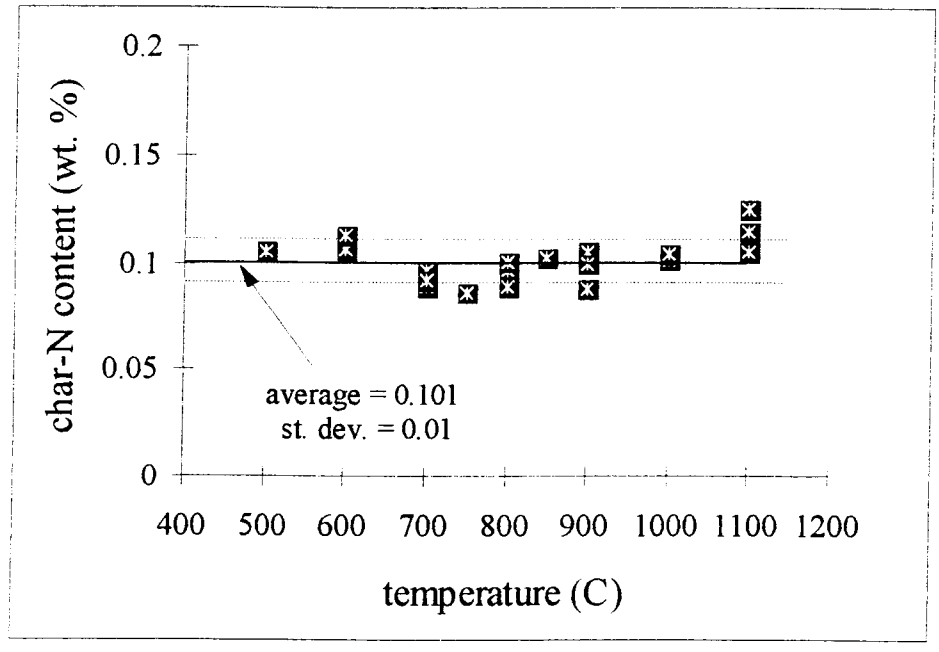


Figure 5.4. Char-N Content as a Function of Temperature
(residence time = 2 seconds)

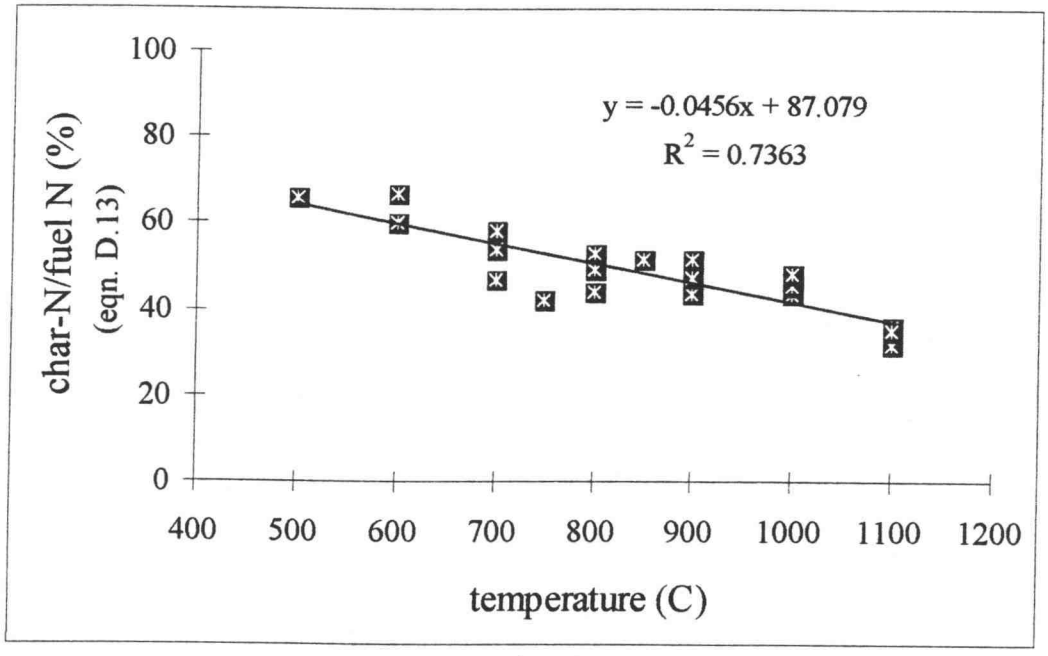


Figure 5.5. Char-N Formation as a Function of Temperature
(residence time = 2 seconds)

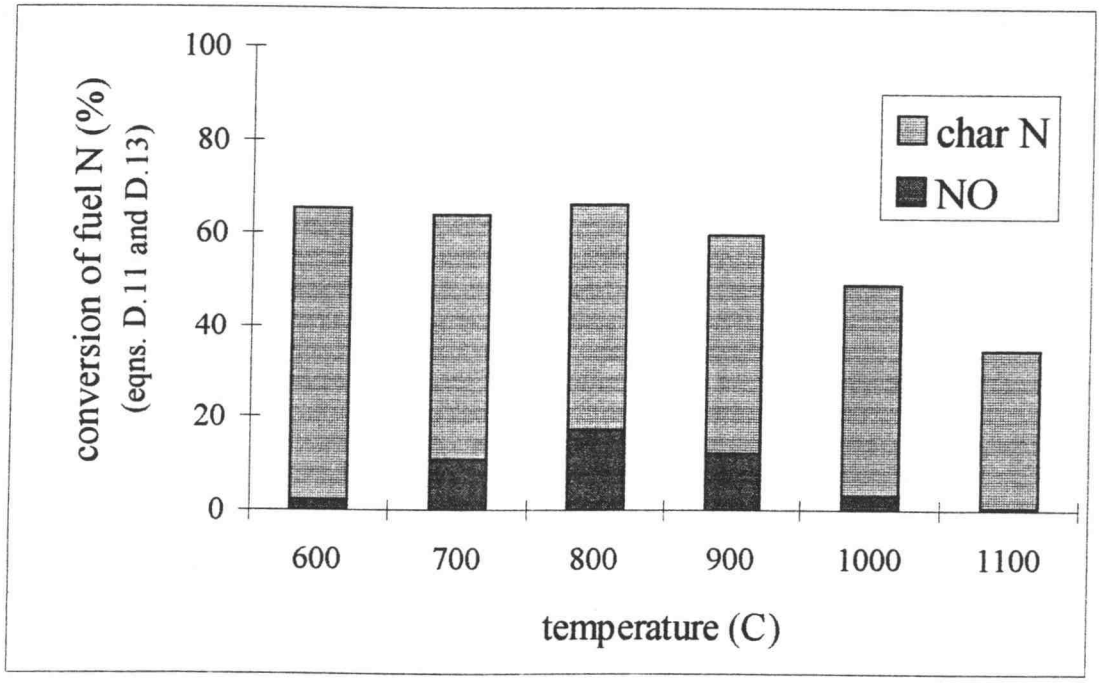


Figure 5.6. NO and Char-N Formation as a Function of Temperature
(residence time = 2 seconds)

5.3 Effects of Residence Time on Nitrogen Evolution

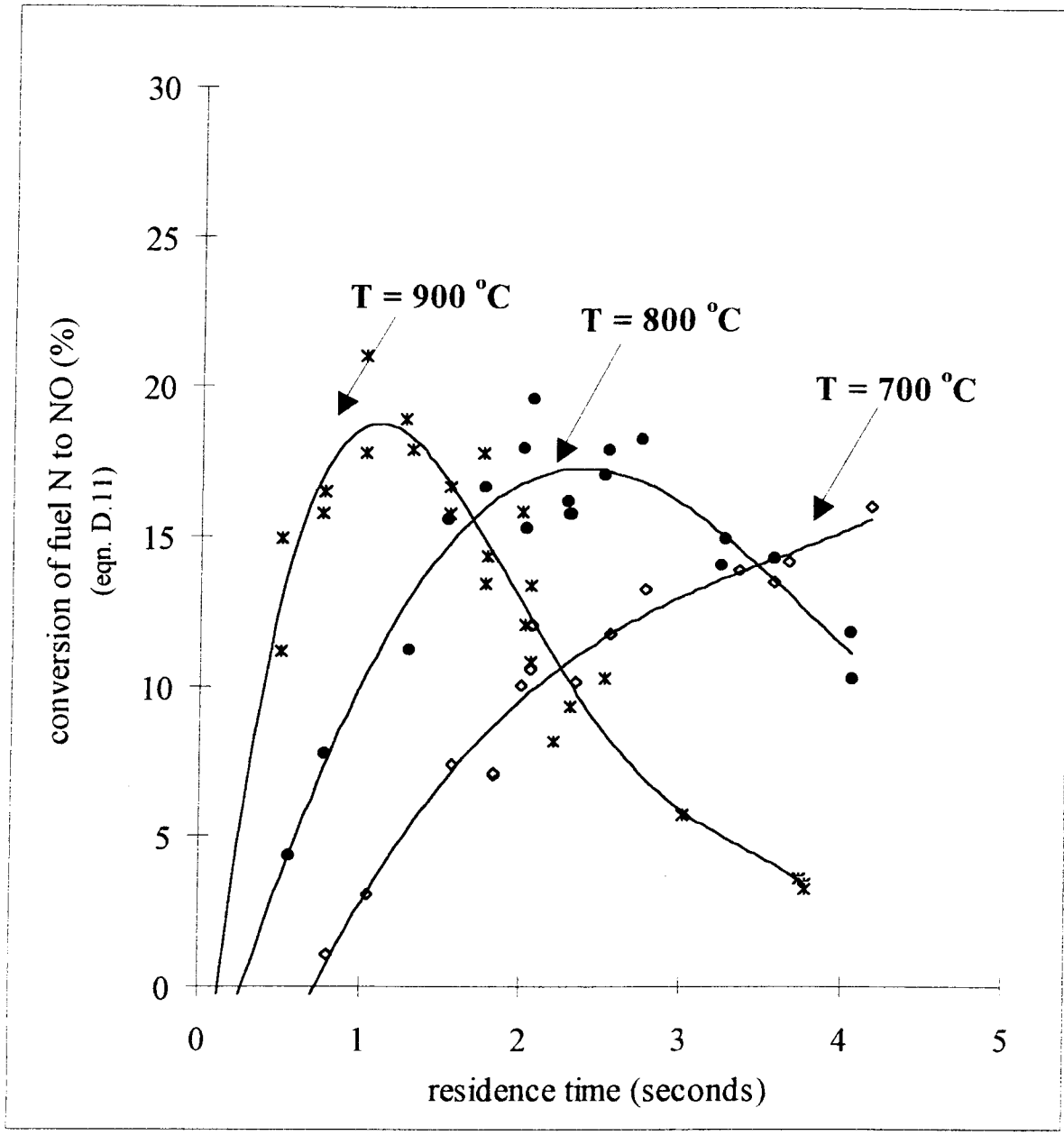
Black liquor pyrolysis experiments were also made at different residence times for furnace temperatures of 700 °C, 800 °C, and 900 °C. The raw data taken during the experiments are included in **Tables** A.3, A.4 and A.5 in **Appendix A** for furnace temperatures 900 °C, 800 °C, and 700 °C, respectively. The corresponding analytical results are summarized in **Tables** D.3, D.4 and D.5 in **Appendix D**. **Figure** 5.7 plots the conversion of fuel N to NO as a function of residence time at the three furnace temperatures. Maxima in conversions to NO were observed at 1 second for 900 °C and 2 seconds for 800 °C. At 700 °C, NO formation was still increasing at 4 seconds and no maximum was observed. The curves shown in **Figure** 5.7 are results from a curve-fitting routine from the Microsoft Excel 5.0 software. The curves were extrapolated to zero to estimate the time at which NO formation started to occur. At 900 °C, the intercept was at 0.1 seconds; at 800 °C, it was at 0.3 seconds; and at 700 °C, it was at 0.7 seconds.

The amount of fuel N that was converted to NH_3 is plotted in **Figure** 5.8 at a furnace temperature of 900 °C and residence times between 0.5 to 2.25 seconds. At residence times longer than 2.25 seconds, the absorption bottles were taken off-line. The results in NH_3 formation were so scattered that no trend was observed as a function of residence time. It was, however, observed that a minimum range of 1 to 7 % of fuel N was converted to NH_3. The NH_3 results for some of the experiments at 700 and 800 °C are in **Tables** D.4 and D.5 in **Appendix D**. The ISE readings recorded during the NH_3 analysis are included in **Table** A.6*b* in **Appendix A**.

The char yields at 700, 800, and 900 °C are plotted in **Figure** 5.9. The char yield decreased with both increasing residence time and furnace temperature. There was a sharp decrease in the char yield during the first 0.5 seconds, after which the char yield decreased steadily. The fitted lines shown in the figure are results from a linear regression

routine from Microsoft Excel 5.0. The slopes of the three fitted lines are almost equal. The difference in the slope is about 0.2 $\frac{\text{g char}}{\text{g BLS sec}}$.

At 900 °C, the total nitrogen contents of the char samples given in **Table** A.7 in **Appendix A** are plotted against the residence time in **Figure** 5.10. The relative weight of char-N to char seemed to be constant with residence time. The average nitrogen content was calculated to be 0.103 wt. % char-N and the standard deviation was 0.008. The amount of fuel N that remained in the char at 900°C is plotted against residence time in **Figure** 5.11. The fraction of fuel N as char-N decreased with residence time.



- **T = 700 °C** : $y = 0.3522\,x^3 - 3.7926\,x^2 + 15.714\,x - 9.5239$; $R^2 = 0.9472$
- **T = 800 °C** : $y = 0.1142\,x^4 + 0.5642\,x^3 - 3.1726\,x^2 + 18.532\,x - 4.8626$; $R^2 = 0.9027$
- **T = 900 °C** : $y = -1.0688\,x^4 + 11.392\,x^3 - 42.189\,x^2 + 57.038\,x - 6.5474$; $R^2 = 0.9149$

Figure 5.7. NO Formation as a Function of Residence Time at 700 °C, 800 °C, and 900 °C

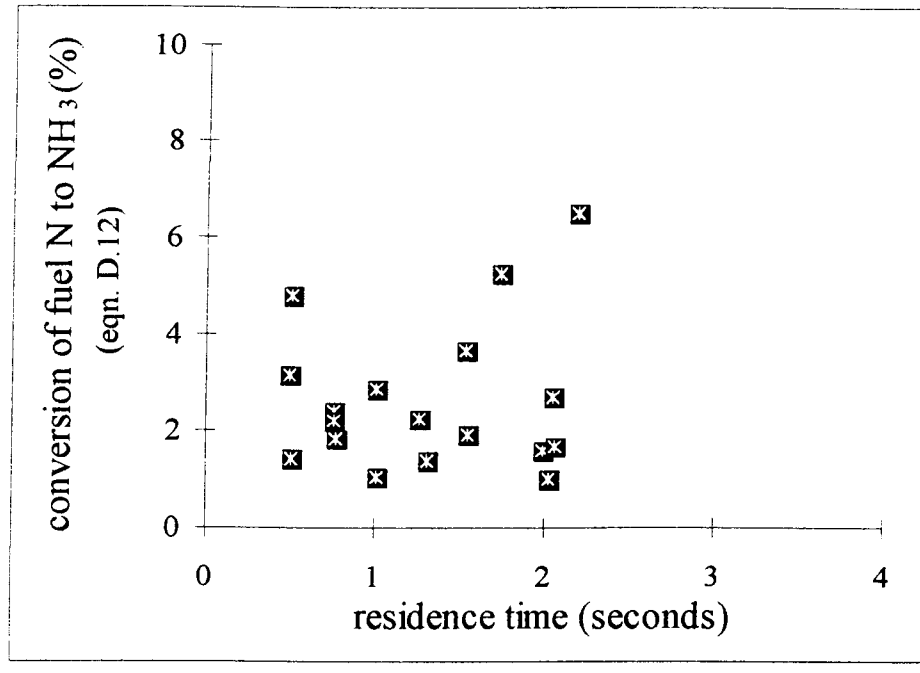
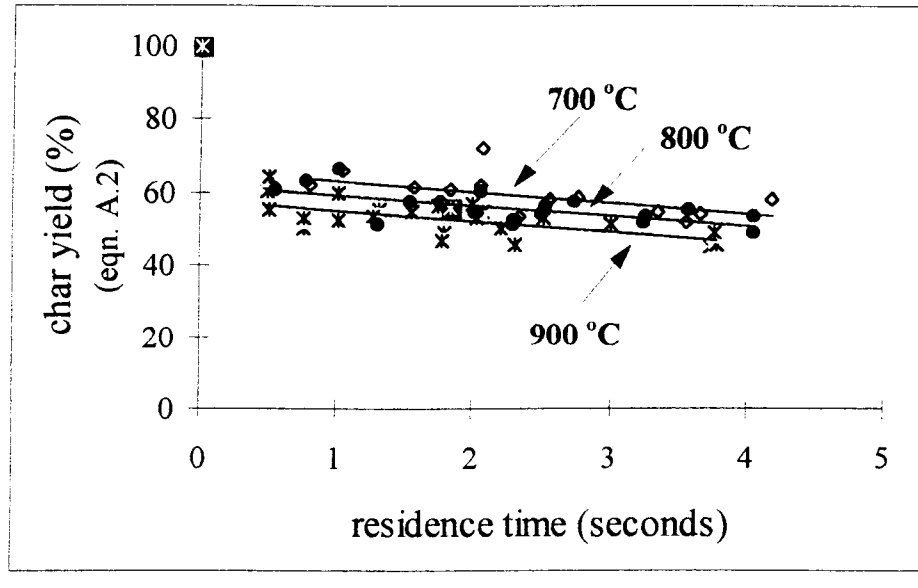


Figure 5.8. NH_3 Formation as a Function of Residence Time at 900 °C



- **T = 700 °C** : $y = -3.0377\,x + 66.488$; $R^2 = 0.3142$
- **T = 800 °C** : $y = -2.8128\,x + 62.23$; $R^2 = 0.4046$
- **T = 900 °C** : $y = -2.9467\,x + 58.13$; $R^2 = 0.3806$

Figure 5.9. Char Yield as a Function of Residence Time at 700 °C, 800 °C, and 900 °C

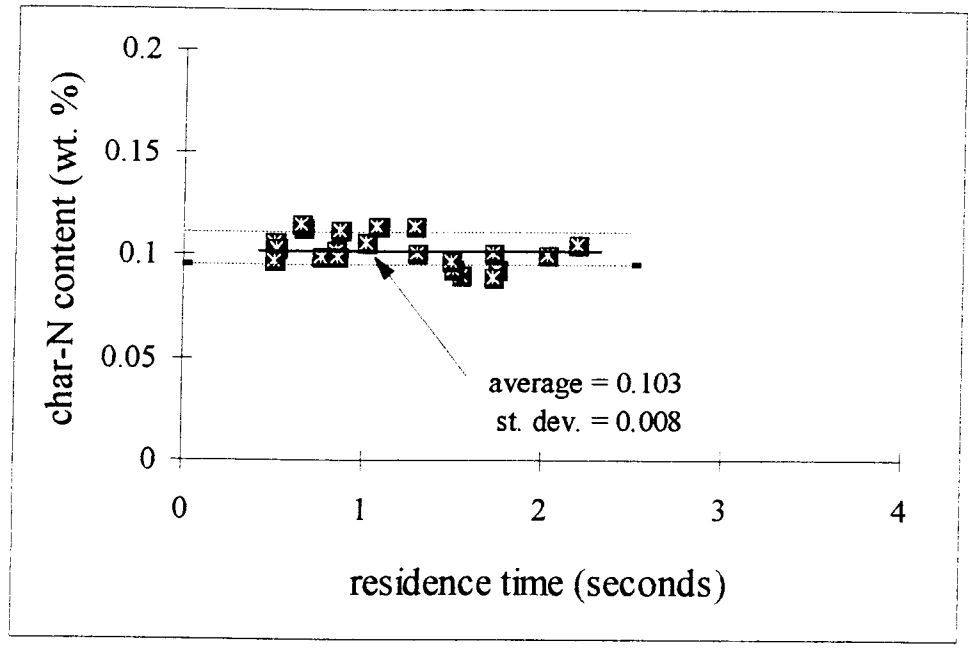


Figure 5.10. Char-N Content as a Function of Residence Time at 900 °C

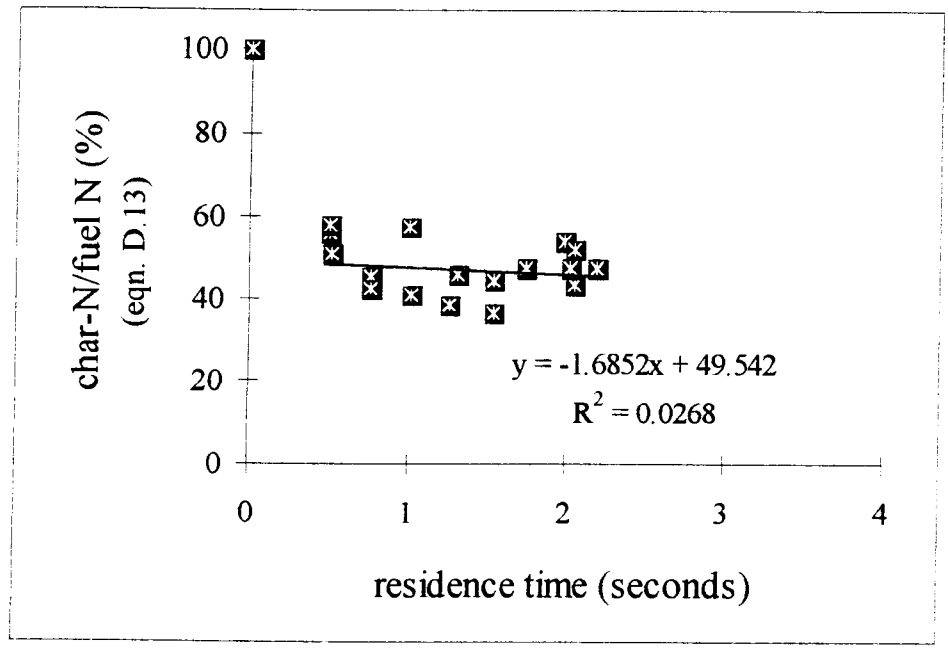


Figure 5.11. Char-N Formation as a Function of Residence Time at 900 °C

CHAPTER 6
DISCUSSION OF RESULTS

6.1 The Nitrogen Release Rate

The nitrogen release rate can be concluded from **Figures** 5.5, 5.6 and 5.11. The fraction of fuel N that remained in the char decreased with increasing temperature and residence time. It was shown in **Figure** 5.5 that at 500 °C, about 35 % of fuel N volatilized in 2 seconds. At 1100 °C, about 65 % volatilized at the same residence time. The sum of NO released and the nitrogen retained in the char, as shown in **Figure** 5.6, seemed to remain constant between 600-800 °C. Although the amount of fuel N that volatilized increased with temperature, the amount of NO formed also increased to the same extent. This suggests that all incremental nitrogen release, that is in addition to the amount released at 600 °C, is NO. At higher temperatures, the amount of N volatilized continued to increase. The net rate of NO formation, however, was being dominated by NO destruction mechanisms.

Figure 5.11 illustrated the fraction of fuel N that remained in the char as a function of residence time at 900 °C. The results indicated that the amount of char-N decreased gradually between 0.5 to 2 seconds. It can also be observed that there was a rapid decrease in char-N at residence times less than 0.5 seconds. This suggests that a major part of nitrogen, may be that which is in the form of amines, was released at shorter residence times (< 0.5 seconds). The gradual change in the char-N content observed at longer residence times may possibly be attributed to the release of heterocyclic nitrogen compounds. From the figure, it seemed that the amount of N released was reaching an asymptotic value. An asymptotic value would indicate that all volatile nitrogen has been released.

The char yield decreased with increasing temperature and residence time as seen in **Figures** 5.3 and 5.9. **Figure** 5.3 showed that the rate of mass loss decrease was significantly affected by temperature. **Figure** 5.9 suggests that significant amounts of volatile species were released below 0.5 seconds residence time, after which the amount of mass loss seemed to decrease gradually with residence time. The quick initial devolatilization agrees with the model developed by Frederick (1990). The model shows that the major part of devolatilization is complete at a residence time less than 0.1 second. In this study, 0.5 seconds was the shortest residence time that could be obtained in the LEFR. Thus, it is unknown how quickly devolatilization occurred during the black liquor pyrolysis studies. However, the small differences in the rates at the longer residence times shown in **Figure** 5.9 suggest that the devolatilization was controlled by a process with a low temperature dependency, *e.g.*, transport processes.

The weight of char-N relative to the weight of char was plotted in **Figures** 5.4 and 5.10. The fraction of nitrogen in the char was approximately constant at 0.10 wt. % in all the experiments. The original content of nitrogen in the black liquor was 0.11 wt. %. The carbon evolution data for some experiments at 900 °C are shown in **Figure** 6.1 (Sricharoenchaikul, 1994). The initial carbon content of the BLS was 35.7 wt. %. The carbon content decreased with increasing residence time. This suggests that the carbon evolution rate is greater than the nitrogen evolution rate. This observation does not agree with the work of Nichols and Lien (1993). They reported that the nitrogen evolution rate was slightly greater than the carbon evolution rate. The results were different possibly because the type of black liquor used was different in both studies. The results in this study, however, agreed with the work of Wornat *et al.* (1994). Wornat and co-workers found that, in biomass char, the nitrogen was retained preferentially to carbon during pyrolysis. They argued that the carbon in biomass chars is aliphatic and the bonds within the aliphatic material are, in general, easily broken. The nitrogen, however, is present within heterocyclic ring structures and aromatic C-N bonds are harder to break. This

argument can be applied to the behavior of fuel nitrogen in the black liquor used in this study. A major part of the nitrogen volatilizing between the residence times of 0.5 to 2 seconds and at 900 °C may have been in the form of heterocyclic nitrogen compounds.

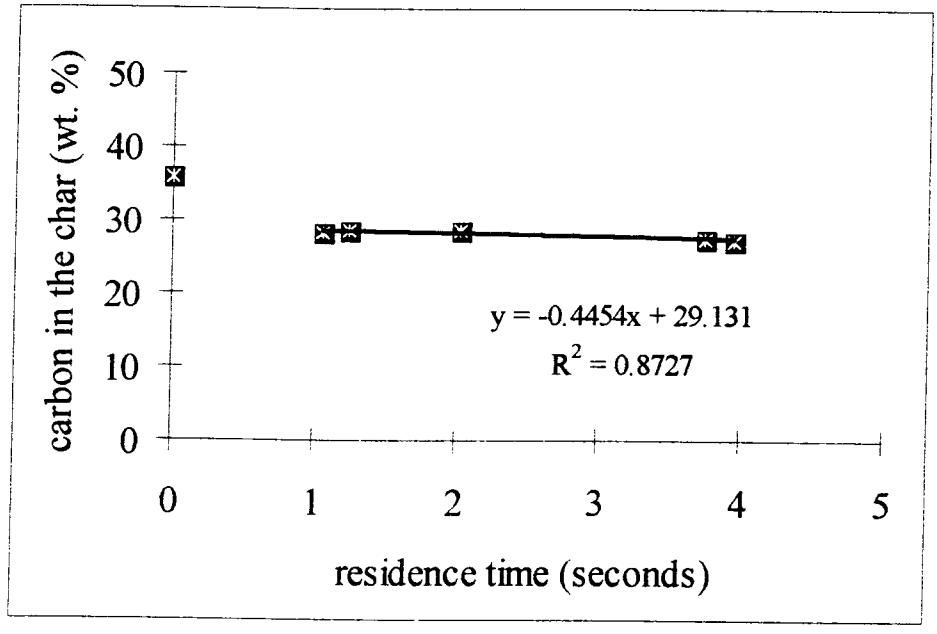


Figure 6.1. Carbon Content as a Function of Residence Time at 900 °C

6.2 Fuel NO Formation in Black Liquor Pyrolysis

The NO was formed from the oxidation of the volatile-N. The only oxygen available during pyrolysis is the oxygen released from the black liquor solids. **Figure** 5.1 illustrated the amount of fuel N that converted to NO. In the figure, the impact of increasing temperature to fuel NO formation during pyrolysis was apparent. The conversion of fuel N to NO initially increased with temperature. However, a maximum was reached and the NO destruction mechanisms dominated. At 2 seconds residence time, the maximum occurred at 800 °C.

The formation of NO at 700, 800 and 900 °C was illustrated in **Figure** 5.7. By extrapolating the data back to zero, it was estimated that at 900 °C, NO started forming at 0.1 seconds; at 800 °C, it occurred at 0.3 seconds; and at 700 °C, it occurred at 0.7 seconds. This suggested that NO formation may start at shorter residence times for higher temperatures. A maximum in NO formation was observed to occur at 2 seconds and 1 second for 800 and 900 °C, respectively. With these results, it can be assumed from **Figure** 5.1 that at 2 seconds, NO destruction at 1000 and 1100 °C was already occurring. Also, at these furnace temperatures, the NO formation and its maximum probably occurred earlier than what was reported for 900 °C. At 700 °C, no maximum occurred and the NO levels were still increasing at 4 seconds. The data suggested that the rate of NO destruction increased with increasing temperature.

In all the experiments, NH_3 was formed. The data shown in **Figures** 5.2 and 5.8 indicate that a minimum range of near 0 to 7 % of fuel N converted to NH_3. Although the data were scattered, it was evident that NH_3 was present even when a major part of NO was reduced. This indicates that at longer residence time (and higher temperature), there may have been no oxygen present to oxidize the NH_3 to NO. There were no conclusive data regarding the trends in NH_3 formation found in this study.

The NO formation pathway during black liquor pyrolysis was illustrated in **Figures** 5.7, 5.8, and 5.11 at 900 °C. There were significant amounts of volatile nitrogen present for NO formation below 0.5 seconds residence time as discussed in the previous section. The volatile nitrogen formed NH_3, after which the NH_3 was oxidized to NO. As the residence time increased, the NO destruction mechanisms started to compete with the NO formation mechanisms. At higher residence times (and higher temperatures), a part of NO probably reacted to form molecular nitrogen. The NO destruction mechanisms may have been due to homogeneous reactions of NO and other gas species or heterogeneous reactions of NO with char. It may also be due to NO-fume reactions as suggested by Nichols and Lien (1993). Preliminary experiments at Oregon State University show that

the NO-fume reactions are slower than the heterogeneous reactions of NO with char (Iisa, 1994). The role of destruction mechanisms during pyrolysis may have been enhanced due to the lack of oxygen needed to oxidize the NH_3 to NO.

In the experiments presented, the maximum amount of NO formed was about 20 % at 800 and 900 °C. As mentioned by Nichols *et al.* (1993), 20 % of the fuel N in the black liquor accounts for the typical levels of NO_x emission in recovery boilers. The typical NO_x emission level was produced in this study for some of the operating conditions used. With this, it can be concluded that it was possible to produce significant levels of NO during the pyrolysis stage. In actual recovery boiler operation in which air is fed to supply oxygen, the maximum NO formed may be significantly higher than the typical emission levels because most or all of the NH_3 is oxidized to NO. However, the NO at the stack outlet may still be about 20 % of the fuel N because some of the NO was probably reduced to molecular nitrogen.

This study was compared to the work of Aho *et al.* (1993). They found that 20 - 60 % of the fuel N volatilized. Only 1 - 2 % of the fuel N content formed NO and a major part of the volatilized nitrogen, 10 - 30 %, formed NH_3 (refer to **Figure** 3.2). The amount of volatilized N in this study varied from 35 - 65 % of the original nitrogen in the black liquor and this agrees well with Aho and co-workers' findings. However, the NO formation was found to be near zero to about 20% at maximum operating conditions. In **Figure** 5.1, less than 1% of NO was formed at 1100°C but in **Figure** 5.7, as much as 20% of NO was formed. The results for NH_3 could not be compared because the results in this study were inconclusive. Nevertheless, a comparison between Aho and co-workers' work and this study is difficult to accomplish because the type of reactor and black liquor used in the two studies were different. Furthermore, the actual residence time of the gases in the tube furnace used by Aho and co-workers is not known. It is possible that in the experiments of Aho *et al.*, more NO was formed but it was reduced as the gases flowed through the reactor and into the gas analyzers. It has been found that, in their reactor, the

particle temperature was probably about 100°C below the furnace temperature because of the colder gas entering the reactor (Wag, 1994).

6.3 Sources of Errors

The variations in results may have been due to the mass loss in the feed system. The black liquor particles accumulated on the walls of the injector and were restricting the flow into the LEFR. During the flushing routine, some of these black liquor particles were pyrolyzed and the char and fume were collected in the cyclone. Although, the additional particulates were accounted for, the assumption made for **eqns.** A.3 and A.4 in **Appendix A** was not necessarily true. The assumption was that the particulates collected during the flushing routine had volatilized to the same extent as during the experiment. Based on **Figure** 5.9, the char yield decreased with increasing residence time. The residence time at maximum primary flow rate was lower than the residence time used in the experiment. Thus, the additional char weight should have been lower than what was recorded. This error causes an overestimation of char yield and underestimation of BL_{actual}. In the worst case, the error in the char yield during the flushing routine was about 10 %. With a maximum of 30 % of BL_{feed} accumulated in the injector, the char yield was overestimated by less than 2 % and the BL_{actual} was underestimated by about 3 %. The error only applies to the operating conditions used in this study. This error is considered insignificant.

The problem regarding mass loss was reduced by collecting the additional char and fume during flushing. However, the amount of black liquor particles exiting the tip of the injector as unpyrolyzed liquor during back-flushing was not collected. There were no available means of collecting the additional black liquor particles during this routine. If these particles were collected, they would have been accounted for as the amount of BL_{feed} that was not fed. The contribution of the additional black liquor particles trapped in the injector to mass loss is currently unknown. It is, however, recommended to disregard

experiments that have calculated mass flow rates less than 0.3 g/min. There may have been substantial mass loss in the injector for these experiments.

The total nitrogen analysis might also be a source of error. The nitrogen content in black liquor and in the char samples was small. The analyses for the samples were at or near the detection limit of the Kjeldahl method. Thus, the accuracy was not very good. As reported in **Table** A.7 in **Appendix A**, some of the duplicate analyses showed differences greater than 0.01 wt. % N. It was uncertain if it was due to the accuracy of the Kjeldahl method used or if the char itself was not uniform. Both are possible. Another total nitrogen analysis method should be used to check the results in this study.

CHAPTER 7
CONCLUSIONS

The conclusions for the nitrogen evolution studies in the LEFR during black liquor pyrolysis in the temperature range of 600 - 1100 °C and residence times of 0.5 to 4.5 seconds are as follows:

- The new experimental procedure presented and used in this study was feasible for nitrogen evolution studies in the LEFR. The absorption technique was, however, found to be inadequate for NH_3 gas sampling.
- A significant amount of the original fuel nitrogen volatilized during black liquor pyrolysis. In the study, about 35 - 65 % of the nitrogen in the black liquor volatilized depending on the temperature and residence time.
- Nitrogen release increased with increasing temperature and residence time.
- NO and NH_3 were formed during black liquor pyrolysis. However, the results for NH_3 formation were inconclusive because the NH_3 released was not successfully measured.
- NO was formed due to the oxidation of NH_3 or other N intermediates. The NO formation rate increased with increasing temperature and residence time.
- A maximum in NO formation as a function of residence time existed because the NO destruction mechanisms were dominant at higher residence times. The NO destruction mechanisms were enhanced by temperature.
- The fraction of fuel N that remained in the char (char-N) decreased with increasing temperature and residence time. However, the relative weight of char-N to the weight of the char remained constant. The content of char-N was approximately equal to the original nitrogen content in black liquor.
- The rate of nitrogen evolution is lower than the rate of carbon evolution.

CHAPTER 8
RECOMMENDATIONS FOR FUTURE WORK

Much work needs to be done to resolve some of the existing problems. Modifications in the LEFR's feed system have been suggested (Sinquefield, 1994). They are the following

- a larger vibration device be installed on the whole feed system to decrease the plugging problems and to ease the flow of the black liquor particles into the LEFR.
- use a cyclone at the tip of injector to further collect the remaining black liquor particles in the injector during back-flushing.

Concerning the nitrogen evolution studies, some methods for analysis need to be further examined or modified.

- The accuracy of the Kjeldahl method has been in question because some of the duplicate analyses yield differences greater than the tolerance value of 0.01 wt %. Thus, the results for total nitrogen analysis in the black liquor and the char samples need to be verified. One possibility is to use the Antek method which is based on burning the material and measuring the resulting NO. This method is currently being evaluated for the determination of nitrogen content in black liquor by the Institute of Paper Science Technology. It is recommended to have the black liquor and char samples from this study, analyzed using the Antek method. A comparison of the results using the Kjeldahl method and the Antek method can determine which method is more appropriate for the total nitrogen analysis.
- Determine the proper method to obtain the NH_3 levels for the LEFR experiments. It was found that NH_3 might have been adsorbing on some surfaces of the LEFR. The

primary work that needs to be done is to determine where the NH_3 is being adsorbed and to resolve this problem. Then, the absorption technique can again be verified for appropriateness. Otherwise, there is a need to acquire an NH_3 gas analyzer instrument. Gas chromatography was found to be inappropriate during some preliminary tests because the resulting NH_3 is at or near the detection limit and the results were not reproducible.

As a continuation of this study, the following recommendations are made:

- resolve the problems in the NH_3 analysis and determine the NH_3 levels during black liquor pyrolysis for the same operating conditions as in this study.
- perform combustion studies for the same black liquor samples and determine the NO formation as a function of furnace temperature, residence time, and oxygen concentration.
- perform experiments using an inert gas such as He or Ar to verify that thermal NO formation is not a contributing factor to the NO levels.
- determine the amount of N_2 formed due to the destruction mechanisms in some of the black liquor pyrolysis and combustion experiments to verify the mass balance closure in the LEFR. This part of the study will be carried out in a batch reactor.
- examine the importance of NO-fume reactions in the NO destruction mechanisms.
- develop a model for the evolution of nitrogen during black liquor pyrolysis and combustion.

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APPENDICES

Appendix A
Raw Data

The total char is derived by adding the weights of the char obtained from the experiment and the char obtained from flushing.

$$char_{total} = char_{ex} + char_{f} \qquad (A.1)$$

where $char_{total}$ = total char weight in grams
$char_{ex}$ = char weight in grams obtained from the experiment
$char_{f}$ = char weight in grams obtained from flushing

The char yield, γ, is given by

$$\gamma = \frac{char_{ex}}{BL_{actual}} * 100\ \% \qquad (A.2)$$

where γ = char yield in percent
BL_{actual} = amount of actual black liquor in grams fed into the LEFR

However, based on the following assumptions

1. $char_{f}$ is a product of the accumulated black liquor particles in the feed system
2. char yield is not affected by the change of residence time

the char yield can also be calculated by

$$\gamma = \frac{char_{total}}{BL_{feed}} * 100\ \% \qquad (A.3)$$

where BL_{feed} = amount of black liquor feed in grams as calculated from before and after "BL + test tube" weights from the raw data

From **eqns.** A.2 and A.3, BL_{actual} is given by

$$BL_{actual} = \frac{char_{ex}}{char_{total}} * BL_{feed} \qquad (A.4)$$

The $char_{total}$ and BL_{actual} for all the experiments are included in **Tables** A.1 through A.5.

Table A.1. Feasibility Studies in the LEFR

DATE	*30-May*	*30-May*	*30-May*	*5-Jun*	*5-Jun*	*6-Jun*	*6-Jun*	*7-Jun*	*7-Jun*	*8-Jun*
EXPERIMENT #	*2*	*3*	*4*	*10*	*11*	*12*	*13*	*15*	*16*	*17*
Data Acquisition Filename	PPY 2	PPY 3	PPY 4	PPY 10	PPY 11	PPY 12	PPY 13	PPY 15	PPY 16	PPY 17
Temperature (C)	900	900	900	700	700	800	800	800	1000	1000
Room Temperature (C)	19.5	19.5	19.5	22.6	22.6	21.2	20.9	22.4	22.4	20.4
Total Feed Gas Flow (l/min)	13	13	13	13	13	13	13	13	13	13
Primary Flow (l/min)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Quench Flow (l/min)	20	20	20	20	20	20	20	20	20	20
Scrubber Flow (l/min)	4	3	4	4	4	4	4	4	4	4
Running Time (min)	5	6	5	4	5	4.5	3	4	5	5
Path length (inches)	17	17	17	17	17	17	17	17	17	17
Black Liquor Feed (g)	2.2668	2.5355	2.3534	1.8021	2.2198	1.8378	1.0746	0.9945	1.7062	2.0857
before (test tube + BL)	19.7208	17.2455	19.567	19.6846	17.8075	19.2189	19.4884	19.272	18.4969	18.2195
after (test tube + BL)	17.454	14.71	17.2136	17.8825	15.5877	17.3811	18.4138	18.2775	16.7907	16.1338
Char weight (g)	1.2219	1.5212	1.179	1.1629	1.4199	1.0153	0.6817	0.5659	0.932	1.1863
Fume (1) weight (g)										
before (filter 1)	0.1476	0.1525	0.149	0.1487	0.1491	0.1474	0.1493	0.1512	0.1465	0.15
after (filter 1 + fume)	0.1499	0.1541	0.1498	0.1497	0.1497	0.1487	0.1502	0.1521	0.1471	0.1508
Fume (2) weight (g)										
before (filter 2)	0.0845	0.0853	0.0837	0.0811	0.0835	0.0825	0.0818	0.0925	0.0941	0.0934
after (filter 2 + fume)	0.0896	0.0892	0.089	0.0835	0.0854	0.0842	0.083	0.0929	0.0957	0.0946
Fume (3) weight (g)										
before (filter 3)	0.2979	0.2992	0.3027	0.2912	0.2967	0.3241	0.3239	0.3391	0.3382	0.3365
after (filter 3 + fume)	0.3349	0.3371	0.3326	0.314	0.3227	0.3497	0.338	0.3557	0.3723	0.3696
HCl solution	150	150	150	150	150	150	150	150	150	150
NO range	2.5 to 10	10	10	10	10	10	10	10	10	10
Comment:	glove bag used from now on			use old NO calibration gas		filter (3) is 5 um nylon	used He in glove bag	filter (3) is back to 0.8 um nylon		
							filter (3) is 5 um nylon			

Table A.1. Feasibility Studies in the LEFR (continued)

DATE	*8-Jun*	*17-Jun*	*17-Jun*	*17-Jun*	*17-Jun*	*17-Jun*	*17-Jun*	*17-Jun*
EXPERIMENT #	*18*	*19*	*20*	*21*	*22*	*23*	*24*	*25*
Data Acquisition Filename	PPY 18	PPY 19	PPY 20	PPY 21	PPY 22	PPY 23	PPY 24	PPY 25
Temperature (C)	1100	850	850	900	900	900	1100	1100
Room Temperature (C)	23.2	22.8	22.6	23.5	23.5	23.4	20.2	20.2
Total Feed Gas Flow (l/min)	13	13	13	13	13	13	13	13
Primary Flow (l/min)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Quench Flow (l/min)	20	20	20	20	20	20	20	20
Scrubber Flow (l/min)	4	4	4	4	-	4	4	4
Running Time (min)	4	5	5.5	5	5	5	5	5
Path length (inches)	17	17	17	17	17	17	17	17
Black Liquor Feed (g)	1.2825	1.0052	0.9932	0.3413	2.0186	2.2991	1.8937	1.9987
before (test tube + BLS)	18.3345	18.9645	21.5443	18.7717	20.795	20.6411	19.9646	18.5374
after (test tube + BLS)	17.052	17.9593	20.5511	18.4304	18.7764	18.342	18.0709	16.5387
Char weight (g)	0.9491	0.4156	0.4166	0.1341	0.8158	1.0414	0.6257	0.7109
Fume (1) weight (g)		-	-	-	-	-	-	-
before (filter 1)	0.1456	-	-	-	-	-	-	-
after (filter 1 + fume)	0.1468	-	-	-	-	-	-	-
Fume (2) weight (g)		0.0012	0.0016	0.0008	0.0007	0.004	0.0139	0.0133
before (filter 2)	0.0837	0.0931	0.0935	0.0933	0.0948	0.0924	0.0929	0.0934
after (filter 2 + fume)	0.0866	0.0943	0.0951	0.0941	0.0955	0.0964	0.1068	0.1067
Fume (3) weight (g)		-	-	-	-	-	-	-
before (filter 3)	0.3406	-	-	-	-	-	-	-
after (filter 3 + fume)	0.3932	-	-	-	-	-	-	-
HCl solution	150	150	150	150	-	150	150	150
NO range	10	10	1000 to 10	10	10	10	10	1000 to 2.5
Comment:	BL feed after wt. is low	no glove box used from now on		use PPY20 NO calib.	teflon tube melted	teflon tube not heated	teflon tube not heated	NO range switched at 1.5 min
								new teflon tube used from now on

Table A.2. Nitrogen Evolution at 2 seconds residence time in the LEFR

DATE	*28-Jun*	*28-Jun*	*28-Jun*	*28-Jun*	*30-Jun*	*30-Jun*	*30-Jun*	*30-Jun*	*30-Jun*
EXPERIMENT #	*57*	*58*	*59*	*60*	*67*	*68*	*70*	*71*	*72*
Data Acquisition Filename	PPY 57	PPY 58	PPY 59	PPY 60	PPY 67	PPY 68	PPY 70	PPY 71	PPY 72
Furnace Temperature (C)	700	700	800	800	1000	1000	1000	1100	1100
Room Temperature (C)	29.2	30.8	31.1	29.9	26.2	28.2	28.2	28	27.1
Total Feed Gas Flow (l/min)	12.6	12.6	11.4	11.4	12.4	12.4	12.4	11.4	11.4
Primary Flow (l/min)	0.109	0.109	0.099	0.099	0.107	0.107	0.107	0.099	0.099
Quench Flow (l/min)	16.8	16.8	15.2	15.2	16.5	16.5	16.5	15.3	15.3
Scrubber Flow (l/min)	4	4	4	4	4.75	5	5	5	5
Running Time (min)	3.75	3.25	5	2.25	3.5	3.5	6	2.5	4.5
Path length (inches)	14	14	14	14	18	18	18	18	18
Black Liquor Feed (g)	2.4657	1.351	2.2841	0.7802	1.1822	1.4094	3.0086	0.6768	1.7883
before (test tube + BLS)	18.6261	19.4328	19.4969	18.9756	19.4353	17.936	19.602	19.069	19.0094
after (test tube + BLS)	16.1604	18.0818	17.2128	18.1954	18.2531	16.5266	16.5934	18.3922	17.2211
Char wt. (g)	1.4635	0.7334	1.2951	0.379	0.5117	0.6212	1.4451	0.177	0.5758
Fume (2) wt. (g)	0.0021	0.0002	0.0025	0.0009	0.0021	0.0012	0.0057	0.0042	
before (filter 2)	0.0935	0.0931	0.0819	0.0822	0.0825	0.0817	0.0819	0.0841	-
after (filter 2 + fume)	0.0956	0.0933	0.0844	0.0831	0.0846	0.0829	0.0876	0.0883	-
Char wt. after flushing (g)	0.3223	0.1058	0.0913	0.0474	0.0509	0.081	0.1113	0.0385	0.0261
Fume (3) wt. after flushing (g)					0.0293	0.0052	0.0173	0.0308	0.0308
before (filter 3)	-	-	-	-	0.0647	0.0601	0.0612	0.0576	0.0576
after (filter 3 + fume)	-	-	-	-	0.094	0.0653	0.0785	0.0884	0.0884
Total char wt. (g)	1.7858	0.8392	1.3864	0.4264	0.5626	0.7022	1.5564	0.2155	0.6019
Actual BLS feed (g)	2.0207	1.1807	2.1337	0.6935	1.0752	1.2468	2.7935	0.5559	1.7108
HCl solution	150	150	140	140	140	140	140	140	140
NO range	10	10	25	25	10	2.5	10	10	10
Comment:					plugged at 3.5 min	NO went above range			forgot to put filter
						scrubber flow turned on after 1 min.			

Table A.2. Nitrogen Evolution at 2 seconds residence time in the LEFR (continued)

DATE	*30-Jun*	*4-Jul*	*4-Jul*	*4-Jul*	*4-Jul*	*4-Jul*	*7-Jun*	*7-Jun*	*7-Jun*
EXPERIMENT #	*74*	*75*	*76*	*77*	*78*	*79*	*90*	*91*	*92*
Data Acquisition Filename	PPY 74	PPY 75	PPY 76	PPY 77	PPY 78	PPY 79	PPY 90	PPY 91	PPY 92
Furnace Temperature (C)	1100	900	850	800	750	700	600	600	500
Room Temperature (C)	27.1	25.5	23.9	23.5	23.4	23.3	27	29	30.1
Total Feed Gas Flow (l/min)	11.4	11.9	12.5	13	13.7	14.4	12	12	13.6
Primary Flow (l/min)	0.099	0.103	0.108	0.113	0.119	0.125	0.104	0.104	0.118
Quench Flow (l/min)	15.3	15.9	16.6	17.4	18.2	19.2	16	16	18.1
Scrubber Flow (l/min)	5	5	5	5	5	5	5	5	5
Running Time (min)	2.5	5	5	5	4.33	5	5	2.5	4
Path length (inches)	18	16	16	16	16	16	12	12	12
Black Liquor Feed (g)	0.9446	2.032	2.2543	2.3625	1.8407	2.2719	2.3471	0.8897	1.841
before (test tube + BLS)	19.2972	19.2532	18.8842	18.8231	19.299	18.9817	19.209	19.0839	19.2787
after (test tube + BLS)	18.3526	17.2212	16.6299	16.4606	17.4583	16.7098	16.8619	18.1942	17.4377
Char wt. (g)	0.307	0.9759	1.1286	1.2175	0.9285	1.1872	1.4655	0.4541	1.1419
Fume (2) wt. (g)	0.006	0.0019	0.0022	0.0025	0.0016	0.002	0.0021	0.0009	0.0006
before (filter 2)	0.0833	0.0836	0.084	0.0831	0.0833	0.0818	0.0814	0.0813	0.0814
after (filter 2 + fume)	0.0893	0.0855	0.0862	0.0856	0.0849	0.0838	0.0835	0.0822	0.082
Char wt. after flushing (g)	0.0121	0.1007	0.1343	0.0772	0.0749	0.1085	0.1698	0.0754	0.1384
Fume (3) wt. after flushing (g)	0	0.0103	0.0087	0.0097	0.0063	0.0066	0.0063	0.0048	0.0054
before (filter 3)	0.0604	0.0579	0.0568	0.0682	0.0668	0.0684	0.0575	0.0638	0.0677
after (filter 3 + fume)	0.0604	0.0682	0.0655	0.0779	0.0731	0.075	0.0638	0.0686	0.0731
Total char wt. (g)	0.3191	1.0766	1.2629	1.2947	1.0034	1.2957	1.6353	0.5295	1.2803
Actual BLS feed (g)	0.9088	1.8419	2.0146	2.2216	1.7033	2.0817	2.1034	0.7630	1.6420
HCl solution	140	140	140	140	140	140	140	140	140
NO range	2.5	25	25	25	25	25	25	10	2.5
Comment:	check scrubber flow time in DA file	scrubber flow turned on after 10 sec							scrubber flow turned on after 5 sec

Table A.3. Nitrogen Evolution at 900 C in the LEFR

DATE	*18-Jun*	*20-Jun*	*20-Jun*	*20-Jun*	*20-Jun*	*20-Jun*	*20-Jun*	*21-Jun*	*21-Jun*
EXPERIMENT #	*26*	*31*	*32*	*33*	*34*	*35*	*36*	*39*	*40*
Data Acquisition Filename	PPY 26	PPY 31	PPY 32	PPY 33	PPY 34	PPY 35	PPY 36	PPY 39	PPY 40
Residence Time (C)	0.85	0.65	0.85	1	1.25	1.5	1.75	1	0.65
Room Temperature (C)	20	26.3	26.3	26.3	26.3	26.3	26.3	26.4	26.4
Total Feed Gas Flow (l/min)	17.7	23.3	17.7	14.1	11.7	10	8.8	14.1	23.3
Primary Flow (l/min)	0.154	0.204	0.154	0.123	0.104	0.088	0.077	0.123	0.204
Quench Flow (l/min)	23.6	31.1	23.6	18.8	15.6	13.3	11.7	18.8	31.1
Scrubber Flow (l/min)	4	4	4	4	4	4	4	4	4
Running Time (min)	6	3	6	6	5	5.75	4.5	5	6
Path length (inches)	10	10	10	10	10	10	10	10	10
Black Liquor Feed (g)	2.488	0.9298	1.9394	2.6667	1.4366	0.6336	1.4864	2.4249	
before (test tube + BLS)	19.0071	19.5077	18.6315	18.2536	18.9308	18.8444	18.4015	18.4433	18.7139
after (test tube + BLS)	16.5191	18.5779	16.6921	15.5869	17.4942	18.2108	16.9151	16.0184	-
Char weight (g)	1.0509	0.378	0.9179	1.4759	0.5191	0.2905	0.7824	1.1821	1.2463
Fume (2) weight (g)	0.0048	0.0009	0.0037	0.0051	0.0037	0.0013	0.0037	0.0045	0.005
before (filter 2)	0.0949	0.0928	0.0934	0.0946	0.094	0.0918	0.0921	0.0939	0.0923
after (filter 2 + fume)	0.0997	0.0937	0.0971	0.0997	0.0977	0.0931	0.0958	0.0984	0.0973
HCl solution	150	150	150	150	150	150	150	150	150
NO range	2.5 to 10	2.5	2.5 to 10	10	25	10	10 to 25	10	2.5
Comment:	new NO calibration gas used from now on	plugged but keep data	start to plug at 5.5 min.		NO flow is at 1.25 scfh Why??	Vp from 91 to 86 and NO decrease to zero	NO range switched at 3 min.	teflon line not heated until after experiment	teflon line not heated until after experiment
			closed at 6 min. but NO has already decreased to zero						forgot to weigh BLS so assume 40 % char yield
			teflon line not heated						

Table A.3. Nitrogen Evolution at 900 C in the LEFR (continued)

DATE	*21-Jun*	*21-Jun*	*21-Jun*	*21-Jun*	*26-Jun*	*26-Jun*	*26-Jun*	*26-Jun*
EXPERIMENT #	*41*	*42*	*43*	*44*	*51*	*52*	*53*	*54*
Data Acquisition Filename	PPY 41	PPY 42	PPY 43	PPY 44	PPY 51	PPY 52	PPY 53	PPY 54
Furnace Temperature (C)	0.85	1.25	1.5	1.75	0.5	0.75	0.75	1
Room Temperature (C)	25.4	25.4	25.4	25.4	27.5	27.5	27.5	27.5
Total Feed Gas Flow (l/min)	17.7	11.7	10	8.8	21	14.1	14.1	10.4
Primary Flow (l/min)	0.154	0.104	0.088	0.077	0.182	0.121	0.121	0.09
Quench Flow (l/min)	23.6	15.6	13.3	11.7	28	18.7	18.7	13.9
Scrubber Flow (l/min)	4	4	4	4	4	4	4	4
Running Time (min)	3	4	3	3	5.5	2.5	4.5	5
Path length (inches)	10	10	10	10	7	7	7	7
Black Liquor Feed (g)	1.1147	1.8053	0.9933	0.6189	2.5776	0.8812	2.2911	1.4029
before (test tube + BLS)	19.0557	19.0508	18.2761	18.0468	18.627	18.2895	18.7235	18.5983
after (test tube + BLS)	17.941	17.2455	17.2828	17.4279	16.0494	17.4083	16.4324	17.1954
Char wt. (g)	0.3296	1.0202	0.3594	0.2366	1.0562	0.1639	1.1639	0.8406
Fume (2) wt. (g)	0.0016	0.0036	0.0027	0.0027	0.0042	0.0007	0.0029	0.0029
before (filter 2)	0.0936	0.095	0.0924	0.0924	0.0937	0.0911	0.0918	0.0837
after (filter 2 + fume)	0.0952	0.0986	0.0951	0.0951	0.0979	0.0918	0.0947	0.0866
Char wt. after flushing (g)	-	-	-	-	0.5091	0.1303	-	-
Fume (3) wt. after flushing (g)								
before (filter 3)	-	-	-	-	-	-	-	-
after (filter 3 + fume)	-	-	-	-	-	-	-	-
Total char wt. (g)	-	-	-	-	1.5653	0.2942	-	-
Actual BLS feed (g)	-	-	-	-	1.7393	0.4909	-	-
HCl solution	150	150	150	150	150	150	150	150
NO range	10	1000 to 10 to 25	25	25	25	25	10	25
Comment:		10 to 25 NO range switched at about 7:17:16			heating tape is re-wrapped on teflon tube	disregard experiment	use the same filter as PPY 52	0.0597 g of BL blown out of injector
		add'l char was brown. Why??			BLS forced by wire from inj. = 0.5091 g			

Table A.3. Nitrogen Evolution at 900 C in the LEFR (continued)

DATE	*27-Jun*	*27-Jun*	*28-Jun*	*28-Jun*	*28-Jun*	*29-Jun*	*29-Jun*	*4-Jul*	*5-Jul*
EXPERIMENT #	*55*	*56*	*61*	*62*	*63*	*64*	*66*	*75*	*81*
Data Acquisition Filename	PPY 55	PPY 56	PPY 61	PPY 62	PPY 63	PPY 64	PPY 66	PPY 75	PPY 81
Furnace Temperature (C)	2	2	1.25	1.5	1.5	2	2	2	1.25
Room Temperature (C)	29.6	29.6	28.9	29.7	29.2	29.8	30.1	25.5	25
Total Feed Gas Flow (l/min)	10.4	10.4	16.7	13.9	13.9	13.4	13.4	11.9	14.3
Primary Flow (l/min)	0.09	0.09	0.145	0.121	0.121	0.129	0.129	0.103	0.124
Quench Flow (l/min)	13.9	13.9	22.3	18.5	18.5	17.9	17.9	15.9	19.1
Scrubber Flow (l/min)	4	4	4	4	4	4.5	4.5	5	5
Running Time (min)	2.5	3	5	3	5	3	4	5	5.5
Path length (inches)	14	14	14	14	14	18	18	16	12
Black Liquor Feed (g)	0.6523	1.101	2.5778	1.0295	2.5706	1.1338	1.8034	2.032	2.6685
before (test tube + BLS)	18.0323	18.1829	19.1856	18.9738	18.8634	18.7127	18.946	19.2532	19.172
after (test tube + BLS)	17.38	17.0819	16.6078	17.9443	16.2928	17.5789	17.1426	17.2212	16.5035
Char wt. (g)	0.304	0.5409	1.2568	0.4644	1.2437	0.5277	0.8264	0.9759	1.2822
Fume (2) wt. (g)	0.0009	0.0007	0.0016	0.0004	0.0017	0.0008	0.0031	0.0019	0.0027
before (filter 2)	0.0917	0.0928	0.0837	0.0852	0.0859	0.0839	0.0826	0.0836	0.082
after (filter 2 + fume)	0.0926	0.0935	0.0853	0.0856	0.0876	0.0847	0.0857	0.0855	0.0847
Char wt. after flushing (g)	0.0551	0.0879	0.1721	0.0982	0.1692	0.0935	0.0829	0.1007	0.1533
Fume (3) wt. after flushing (g)			0.0106	0.0512	0.034	0.0063	0.003	0.0103	0.0109
before (filter 3)	-	-	0.0715	0.0391	0.0568	0.0571	0.0666	0.0579	0.0573
after (filter 3 + fume)	-	-	0.0821	0.0903	0.0908	0.0634	0.0696	0.0682	0.0682
Total char wt. (g)	0.3591	0.6288	1.4289	0.5626	1.4129	0.6212	0.9093	1.0766	1.4355
Actual BLS feed (g)	0.5522	0.9471	2.2673	0.8498	2.2628	0.9631	1.6390	1.8419	2.3835
HCl solution	150	150	140	140	140	140	140	140	140
NO range	25	25	10	1000 to 10	10	25	25	25	25
Comment:	flush feed system at high Vp	flush from now on	new absorption bottle used	NO range switched at 15 sec.		plugged at 3 min	plugged at 4 min	scrubber flow turned on after 10 sec	
	collect char and fume at flushing	plugged				scrubber flow on at 1 min.			

Table A.3. Nitrogen Evolution at 900 C in the LEFR (continued)

DATE	*6-Jul*	*7-Jul*	*7-Jul*	*7-Jul*	*7-Jul*	*7-Jul*	*13-Jul*	*13-Jul*	*13-Jul*
EXPERIMENT #	*82*	*93*	*94*	*95*	*96*	*98*	*104*	*106*	*107*
Data Acquisition Filename	PPY 82	PPY 93	PPY 94	PPY 95	PPY 96	PPY 98	PPY 104	PPY 106	PPY 107
Furnace Temperature (C)	1.75	0.5	0.75	0.75	0.5	1	1.75	1.75	2.25
Room Temperature (C)	25	28.9	28.1	28.3	27.2	31.5	28	30.3	31.4
Total Feed Gas Flow (l/min)	10.2	21	14	14	21	10.4	17.2	17.2	13.4
Primary Flow (l/min)	0.088	0.182	0.121	0.121	0.182	0.09	0.149	0.149	0.116
Quench Flow (l/min)	13.6	28	18.7	18.7	28	13.9	22.9	22.9	17.9
Scrubber Flow (l/min)	5	5	5	5	5	5	5	5	5
Running Time (min)	3.5	5	3	4.5	6	4	5	4.5	3
Path length (inches)	12	7	7	7	7	7	20	20	20
Black Liquor Feed (g)	1.3635	2.2874	0.9948	1.8784	2.7516	1.0195	2.3007	1.869	1.2141
before (test tube + BLS)	18.986	19.2004	18.9546	19.2288	18.9138	19.1254	19.1719	19.4713	18.9393
after (test tube + BLS)	17.6225	16.913	17.9598	17.3504	16.1622	18.1059	16.8712	17.6023	17.7252
Char wt. (g)	0.7039	1.0083	0.4258	0.8556	1.2238	0.4699	1.0172	0.7792	0.4722
Fume (2) wt. (g)	0.0015	0.0018	0.0018	0.0026	0.003	0.0021	0.0019	0.0015	0.0009
before (filter 2)	0.0813	0.0813	0.0817	0.0812	0.0808	0.0822	0.0819	0.0811	0.0817
after (filter 2 + fume)	0.0828	0.0831	0.0835	0.0838	0.0838	0.0843	0.0838	0.0826	0.0826
Char wt. after flushing (g)	0.0687	0.2539	0.0729	0.1389	0.5425	0.066	0.1261	0.1377	0.0832
Fume (3) wt. after flushing (g)	0.0068	-	-	0.0108	-	0.009	0.0023	0.008	0.005
before (filter 3)	0.0577	-	-	0.0566	-	0.056	0.0642	0.0574	0.0567
after (filter 3 + fume)	0.0645	-	-	0.0674	-	0.065	0.0665	0.0654	0.0617
Total char wt. (g)	0.7726	1.2622	0.4987	0.9945	1.7663	0.5359	1.1433	0.9169	0.5554
Actual BLS feed (g)	1.2423	1.8273	0.8494	1.6160	1.9065	0.8939	2.0469	1.5883	1.0322
HCl solution	140	140	140	140	140	140	-	-	-
NO range	25	-	-	25	10	25	25	25	25
Comment:	used 0-10 mass flow meter								
	change scale factor in DA								

Table A.3. Nitrogen Evolution at 900 C in the LEFR (continued)

DATE	*13-Jul*	*13-Jul*	*17-Jul*	*17-Jul*	*17-Jul*	*17-Jul*
EXPERIMENT #	*108*	*109*	*125*	*126*	*127*	*128*
Data Acquisition Filename	PPY 108	PPY 109	PPY 125	PPY 126	PPY 127	PPY 128
Furnace Temperature (C)	2.5	1.75	3	3.75	3.75	3.75
Room Temperature (C)	29.6	28.4	30.5	31.6	32.5	30.9
Total Feed Gas Flow (l/min)	12	17.2	15	12	12	12
Primary Flow (l/min)	0.104	0.149	0.13	0.104	0.104	0.104
Quench Flow (l/min)	16	22.9	20	16	16	16
Scrubber Flow (l/min)	5	5	5	5	5	5
Running Time (min)	5	3.5	3	3	2	2.5
Path length (inches)	20	20	30	30	30	30
Black Liquor Feed (g)	2.4213	1.3048	1.5374	1.4367	0.8464	0.9677
before (test tube + BLS)	19.099	19.0152	20.7897	18.9141	20.2434	18.224
after (test tube + BLS)	16.6777	17.7104	19.2523	17.4774	19.397	17.2563
Char wt. (g)	1.1934	0.5318	0.6413	0.5281	0.3194	0.4031
Fume (2) wt. (g)	0.0022	0.0009	-	-	-	-
before (filter 2)	0.0812	0.081	-	-	-	-
after (filter 2 + fume)	0.0834	0.0819	-	-	-	-
Char wt. after flushing (g)	0.0903	0.0824	0.1452	0.1173	0.069	0.0738
Fume (3) wt. after flushing (g)	0.0087	0.0064	-	-	-	-
before (filter 3)	0.0569	0.0571	-	-	-	-
after (filter 3 + fume)	0.0656	0.0635	-	-	-	-
Total char wt. (g)	1.2837	0.6142	0.7865	0.6454	0.3884	0.4769
Actual BLS feed (g)	2.2510	1.1298	1.2536	1.1756	0.6960	0.8179
HCl solution	-	-	-	-	-	-
NO range	10	10	10	25	10	10
Comment:						

Table A.4. Nitrogen Evolution at 800 C in the LEFR

DATE	*28-Jun*	*28-Jun*	*4-Jul*	*6-Jul*	*6-Jul*	*6-Jul*	*6-Jul*	*6-Jul*	*11-Jul*
EXPERIMENT #	*59*	*60*	*77*	*83*	*84*	*85*	*86*	*87*	*101*
Data Acquisition Filename	PPY 59	PPY 60	PPY 77	PPY 83	PPY 84	PPY 85	PPY 86	PPY 87	PPY 101
Residence Time (C)	800	800	800	1.5	1.75	1.25	1.25	1.25	1
Room Temperature (C)	31.1	29.9	23.5	29.4	29.8	28.4	28.6	28.6	31.5
Total Feed Gas Flow (l/min)	11.4	11.4	13	13	11.4	15.6	15.6	15.6	11.4
Primary Flow (l/min)	0.099	0.099	0.113	0.113	0.099	0.135	0.135	0.135	0.099
Quench Flow (l/min)	15.2	15.2	17.4	17.3	15.2	20.8	20.8	20.8	15.2
Scrubber Flow (l/min)	4	4	5	5	5	5	5	5	5
Running Time (min)	5	2.25	5	4	5	2.2	2.2	4.5	5
Path length (inches)	14	14	16	12	12	12	12	12	7
Black Liquor Feed (g)	2.2841	0.7802	2.3625	1.7493	2.4662	0.8202	0.6478	1.8779	2.199
before (test tube + BLS)	19.4969	18.9756	18.8231	19.541	18.9563	19.5307	19.3996	19.6609	19.5404
after (test tube + BLS)	17.2128	18.1954	16.4606	17.7917	16.4901	18.7105	18.7518	17.783	17.3414
Char wt. (g)	1.2951	0.379	1.2175	0.8928	1.3243	0.3168	0.2491	0.8358	1.3161
Fume (2) wt. (g)	0.0025	0.0009	0.0025	0.0012	0.0031	0.0008	0.0013	0.0018	0.0026
before (filter 2)	0.0819	0.0822	0.0831	0.0821	0.0832	0.0819	0.0827	0.0833	0.0822
after (filter 2 + fume)	0.0844	0.0831	0.0856	0.0833	0.0863	0.0827	0.084	0.0851	0.0848
Char wt. after flushing (g)	0.0913	0.0474	0.0772	0.1194	0.1019	0.0915	0.0551	0.1249	0.1476
Fume (3) wt. after flushing (g)			0.0097	0.0074	0.0077	0.0052	0.0055	0.0103	0.0068
before (filter 3)	-	-	0.0682	0.0648	0.0649	0.0569	0.0568	0.0567	0.0578
after (filter 3 + fume)	-	-	0.0779	0.0722	0.0726	0.0621	0.0623	0.067	0.0646
Total char wt. (g)	1.3864	0.4264	1.2947	1.0122	1.4262	0.4083	0.3042	0.9607	1.4637
Actual BLS feed (g)	2.1337	0.6935	2.2216	1.5430	2.2900	0.6364	0.5305	1.6338	1.9773
HCl solution	140	140	140	140	140	140	140	140	140
NO range	25	25	25	25	25	25	10	10	25
Comment:						teflon line heated after experiment	same fume filter (2) as PPY85	NH3 line on at 30 s	

Table A.4. Nitrogen Evolution at 800 C in the LEFR (continued)

DATE	*11-Jul*	*11-Jul*	*14-Jul*	*14-Jul*	*14-Jul*	*14-Jul*	*14-Jul*	*14-Jul*	*16-Jul*
EXPERIMENT #	*102*	*103*	*110*	*111*	*112*	*113*	*115*	*116*	*122*
Data Acquisition Filename	PPY 102	PPY 103	PPY 110	PPY 111	PPY 112	PPY 113	PPY 115	PPY 116	PPY 122
Residence Time (C)	0.75	0.5	2.75	2.25	2.25	2.25	2.5	2.5	3.25
Room Temperature (C)	31.8	30.5	27	27.6	29.4	30.5	30.4	29.9	27.4
Total Feed Gas Flow (l/min)	15.2	21	11.9	14.5	14.5	14.5	13.1	13.1	15.2
Primary Flow (l/min)	0.132	0.182	0.103	0.114	0.114	0.114	0.114	0.114	0.132
Quench Flow (l/min)	20.3	28	15.9	17.5	17.5	17.5	17.5	17.5	20.3
Scrubber Flow (l/min)	5	5	-	-	-	-	-	-	-
Running Time (min)	4.5	5	4.5	4.5	4.5	5	5.5	5	2.5
Path length (inches)	7	7	20	20	20	20	20	20	30
Black Liquor Feed (g)	2.0576	2.3163	1.9529	1.7792	1.6124	2.2663	2.2263	2.426	0.9194
before (test tube + BLS)	18.6854	19.3642	19.3106	19.0747	19.7567	19.2289	19.5753	19.625	18.9151
after (test tube + BLS)	16.6278	17.0479	17.3577	17.2955	18.1443	16.9626	17.349	17.199	17.9957
Char wt. (g)	1.1241	1.1339	1.0387	0.7922	0.7143	0.9937	1.2174	1.1791	0.3672
Fume (2) wt. (g)	0.0021	0.0029	-	-	-	-	-	-	-
before (filter 2)	0.0821	0.0818	-	-	-	-	-	-	-
after (filter 2 + fume)	0.0842	0.0847	-	-	-	-	-	-	-
Char wt. after flushing (g)	0.1765	0.2731	0.0916	0.139	0.1319	0.1696	0.041	0.13	0.0909
Fume (3) wt. after flushing (g)	-	-	-	-	-	-	-	-	-
before (filter 3)	-	-	-	-	-	-	-	-	-
after (filter 3 + fume)	-	-	-	-	-	-	-	-	-
Total char wt. (g)	1.3006	1.407	1.1303	0.9312	0.8462	1.1633	1.2584	1.3091	0.4581
Actual BLS feed (g)	1.7784	1.8667	1.7946	1.5136	1.3611	1.9359	2.1538	2.1851	0.7370
HCl solution	140	140/110	-	-	-	-	-	-	-
NO range	10	10	25	25	25	25	25	25	25
Comment:	22 seconds delayed on DA	2 absorption bottles used					feeder is not feeding properly		
							NO is fluctuating		

Table A.4. Nitrogen Evolution at 800 C in the LEFR (continued)

DATE	*16-Jul*	*16-Jul*	*19-Jul*	*19-Jul*	*19-Jul*	*19-Jul*
EXPERIMENT #	*123*	*124*	*134*	*135*	*136*	*137*
Data Acquisition Filename	PPY 123	PPY 124	PPY 134	PPY 135	PPY 136	PPY 137
Residence Time (C)	3.25	4	4	3.5	3.25	3.25
Room Temperature (C)	28.4	31.3	33.6	31.5	31.2	31.6
Total Feed Gas Flow (l/min)	15.2	12.3	12.3	14	15.2	15.2
Primary Flow (l/min)	0.132	0.107	0.107	0.121	0.132	0.132
Quench Flow (l/min)	20.3	16.4	16.4	18.7	20.3	20.3
Scrubber Flow (l/min)	-	-	-	-	-	-
Running Time (min)	5	3	4	3	2.5	2.5
Path length (inches)	30	30	30	30	30	30
Black Liquor Feed (g)	2.453	1.1224	1.719	1.354	0.7673	1.0405
before (test tube + BLS)	19.3508	18.7112	18.6067	19.3041	18.9411	19.2855
after (test tube + BLS)	16.8978	17.5888	16.8877	17.9501	18.1738	18.245
Char wt. (g)	1.1189	0.4541	0.7336	0.6011	0.3193	0.4327
Fume (2) wt. (g)	-	-	-	-	-	-
before (filter 2)	-	-	-	-	-	-
after (filter 2 + fume)	-	-	-	-	-	-
Char wt. after flushing (g)	0.1944	0.0976	0.19	0.1458	0.0541	0.1086
Fume (3) wt. after flushing (g)	-	-	-	-	-	-
before (filter 3)	-	-	-	-	-	-
after (filter 3 + fume)	-	-	-	-	-	-
Total char wt. (g)	1.3133	0.5517	0.9236	0.7469	0.3734	0.5413
Actual BLS feed (g)	2.0899	0.9238	1.3654	1.0897	0.6561	0.8317
HCl solution	-	-	-	-	-	-
NO range	25	25	25	25	10	10
Comment:	feeder is not feeding properly					

Table A.5. Nitrogen Evolution at 700 C in the LEFR

DATE	*28-Jun*	*28-Jun*	*4-Jul*	*6-Jul*	*6-Jul*	*11-Jul*	*11-Jul*	*14-Jul*	*14-Jul*
EXPERIMENT #	*57*	*58*	*79*	*88*	*89*	*99*	*100*	*117*	*118*
Data Acquisition Filename	PPY 57	PPY 58	PPY 79	PPY 88	PPY 89	PPY 99	PPY 100	PPY 117	PPY 118
Residence Time (C)	2	2	2	1.5	1.75	1	0.75	2.5	1.75
Room Temperature (C)	29.2	30.8	23.3	28.6	27.3	29.5	30.5	27.4	26.8
Total Feed Gas Flow (l/min)	12.6	12.6	14.4	14.1	12.1	12.3	16	14.2	20
Primary Flow (l/min)	0.109	0.109	0.125	0.122	0.105	0.107	0.139	0.123	0.174
Quench Flow (l/min)	16.8	16.8	19.2	18.8	16.1	16.4	21.3	18.9	26.7
Scrubber Flow (l/min)	4	4	5	5	-	5	5	-	-
Running Time (min)	3.75		5	5	5	3.5	3	5	5
Path length (inches)	14	14	16	12	12	7	7	20	20
Black Liquor Feed (g)	2.4657	1.351	2.2719	2.4374	1.2346	1.4489	1.5066	2.3209	2.2973
before (test tube + BLS)	18.6261	19.4328	18.9817	19.0272	18.9882	18.7518	18.872	19.4497	19.3125
after (test tube + BLS)	16.1604	18.0818	16.7098	16.5898	17.7536	17.3029	17.3654	17.1288	17.0152
Char wt. (g)	1.4635	0.7334	1.1872	1.3427	0.6716	0.8436	0.7992	1.1772	1.0422
Fume (2) wt. (g)	0.0021	0.0002	0.002	0.0021	0.0015	0.0012	0.0009	-	-
before (filter 2)	0.0935	0.0931	0.0818	0.0821	0.0818	0.0825	0.0818	-	-
after (filter 2 + fume)	0.0956	0.0933	0.0838	0.0842	0.0833	0.0837	0.0827	-	-
Char wt. after flushing (g)	0.3223	0.1058	0.1085	0.1605	0.084	0.1141	0.1377	0.1706	0.249
Fume (3) wt. after flushing (g)			0.0066	0.0064	0.0064	-	0.0045	-	-
before (filter 3)	-	-	0.0684	0.057	0.0625	-	0.0571	-	-
after (filter 3 + fume)	-	-	0.075	0.0634	0.0689	-	0.0616	-	-
Total char wt. (g)	1.7858	0.8392	1.2957	1.5032	0.7556	0.9577	0.9369	1.3478	1.2912
Actual BLS feed (g)	2.0207	1.1807	2.0817	2.1772	1.0973	1.2763	1.2852	2.0271	1.8543
HCl solution	150	150	140	140	-	140	140	-	-
NO range	10	10	25	25	25	25	2.5	25	10
Comment:					didn't keep HCL soln.	teflon line heated at the end			
					Vp fluctuates				

Table A.5. Nitrogen Evolution at 700 C in the LEFR (continued)

DATE	*14-Jul*	*14-Jul*	*17-Jul*	*19-Jul*	*19-Jul*	*19-Jul*
EXPERIMENT #	*119*	*120*	*129*	*130*	*132*	*133*
Data Acquisition Filename	PPY 119	PPY 120	PPY 129	PPY 130	PPY 132	PPY 133
Residence Time (C)	2.75	2.25	3.5	4	3.5	3.25
Room Temperature (C)	26.4	25.3	28.4	36	34.2	33.9
Total Feed Gas Flow (l/min)	12.9	15.7	15.2	13.3	15.2	16.5
Primary Flow (l/min)	0.112	0.136	0.132	0.114	0.132	0.143
Quench Flow (l/min)	17.2	20.9	20.3	17.7	20.3	22
Scrubber Flow (l/min)	-	-	-	-	-	-
Running Time (min)	3	5	2.5	4	5	2.5
Path length (inches)	20	20	30	30	30	30
Black Liquor Feed (g)	1.2421	2.2505	1.1045	1.9257	2.4506	1.0441
before (test tube + BLS)	19.2326	19.5579	19.2554	19.0736	19.0768	19.0925
after (test tube + BLS)	17.9905	17.3074	18.1509	17.1479	16.6262	18.0484
Char wt. (g)	0.6266	1.0803	0.4772	0.9479	1.0787	0.4483
Fume (2) wt. (g)	-	-	-	-	-	-
before (filter 2)	-	-	-	-	-	-
after (filter 2 + fume)	-	-	-	-	-	-
Char wt. after flushing (g)	0.106	0.131	0.0971	0.1756	0.2536	0.1224
Fume (3) wt. after flushing (g)	-	-	-	-	-	-
before (filter 3)	-	-	-	-	-	-
after (filter 3 + fume)	-	-	-	-	-	-
Total char wt. (g)	0.7326	1.2113	0.5743	1.1235	1.3323	0.5707
Actual BLS feed (g)	1.0624	2.0071	0.9178	1.6247	1.9841	0.8202
HCl solution	-	-	-	-	-	-
NO range	25	25	10	25	25	10
Comment:					NO zero too high	

Table A.6*a*. NH_3 Calibration

mL standard solution added	ppm NH3	mV reading					
		11-Jun	25-Jun	2-Jul	3-Jun	9-Jul	12-Jul
0	0	109	87.5	66	72	67	67
0.1	0.01		81	57	62	60	59.5
0.2	0.02	81	75.5	51	55	53	53
0.4	0.04	67	68	43	45	44	44
0.6	0.06	58		37	37	36.5	37
0.8	0.08		59				
1	0.1	46.5		28	28	27	28
1.2	0.12	19.5	51.5				
2	0.2			14	13	12	13
2.2	0.22		40.5				
3	0.29				3.5	3	
3.2	0.31		32				
4	0.39					-3	

Table A.6*b*. NH_3 Analysis

DATE	RUN	mV reading	ppm NH3	mL solution	total mg NH3	Comment
11-Jun	2	38	0.12	150	0.0186	old solution
	3	49.5	0.09	150	0.0130	old solution
	4	43	0.11	150	0.0160	old solution
	10	75	0.03	150	0.0040	
	11	73	0.03	150	0.0045	
	12	52	0.08	150	0.0120	
	13	68	0.04	150	0.0060	
	15	76	0.03	150	0.0038	
	16	66	0.04	150	0.0066	
	17	54	0.07	150	0.0111	
	18	78	0.02	150	0.0033	
25-Jun	26	87	0.00	150	0.0001	
	31	89	0.00	150	-0.0002	
	32	70	0.03	150	0.0052	
	33	63	0.06	150	0.0089	
	34	71.5	0.03	150	0.0045	
	35	85	0.00	150	0.0005	
	36	62	0.06	150	0.0096	
	39	73	0.03	150	0.0039	
	40	83	0.01	150	0.0010	
	41	82	0.01	150	0.0012	
	42	69.5	0.04	150	0.0054	

Table A.6*b*. NH_3 Analysis (continued)

DATE	RUN	mV reading	ppm NH3	mL solution	total mg NH3	Comment
25-Jun	43	81	0.01	150	0.0014	
(continued)	44	84	0.00	150	0.0007	
2-Jul	51	42	0.04	150	0.0065	
	53	33	0.08	150	0.0116	
results	54	21	0.14	150	0.0218	
are not	55	45	0.03	150	0.0051	
good so	55	38	0.06	150	0.0084	duplicate
disregard	56	16	0.18	150	0.0271	
	56	13	0.21	150	0.0308	duplicate
	57	40	0.05	150	0.0073	
	58	30	0.09	150	0.0135	
	59	20	0.15	140	0.0210	
	59	22	0.14	140	0.0191	same sample
	60	25	0.12	140	0.0165	
	60	19	0.16	140	0.0220	duplicate
	60	3	0.31	140	0.0430	same sample
3-Jul	51	45	0.04	150	0.0059	
	53	42	0.05	150	0.0069	
results	54	38	0.06	150	0.0087	
are good	55	54	0.02	150	0.0032	
so take	56	55	0.02	150	0.0033	
this data	57	51	0.03	150	0.0040	
	58	52	0.02	150	0.0037	
	59	36	0.06	140	0.0091	
	60	53.5	0.02	140	0.0041	
	61	49	0.03	140	0.0042	
	62	49.5	0.03	140	0.0041	
	63	40	0.05	140	0.0073	
	64	55	0.02	140	0.0028	
	66	18	0.16	140	0.0223	
	67	55	0.02	140	0.0028	
	68	59	0.01	140	0.0021	
	70	35	0.07	140	0.0096	
	71	38	0.06	140	0.0081	
	72	41.5	0.05	140	0.0067	
	74	56.5	0.02	140	0.0025	

Table A.6*b*. NH_3 Analysis (continued)

DATE	RUN	mV reading	ppm NH3	mL solution	total mg NH3	Comment
9-Jul	75	48	0.03	140	0.0043	
	76	44	0.04	140	0.0056	
	77	50	0.03	140	0.0037	
	78	43	0.04	140	0.0060	
	79	50	0.03	140	0.0037	
	81	32	0.08	140	0.0108	
	82	21	0.13	140	0.0182	
	83	20	0.14	140	0.0190	
	84	20	0.14	140	0.0190	
	85	39	0.05	140	0.0076	
	86	45	0.04	140	0.0053	
	87	38	0.06	140	0.0080	
	88	46	0.04	140	0.0050	
	90	38	0.06	140	0.0080	
	91	56	0.01	140	0.0021	
	92	50	0.03	140	0.0037	
	93	30	0.09	140	0.0119	
	94	48.5	0.03	140	0.0042	
	95	40	0.05	140	0.0072	
	96	50	0.03	140	0.0037	
	98	54	0.02	140	0.0026	
	19	49	0.03	150	0.0043	
	20	49	0.03	150	0.0043	
	21	52	0.02	150	0.0033	
	23	44	0.04	150	0.0060	
	24	50	0.03	150	0.0040	
	25	0	0.34	150	0.0506	
12-Jul	99	35	0.07	140	0.0096	
	100	58	0.01	140	0.0017	
	101	50	0.03	140	0.0036	
	102	56	0.01	140	0.0021	
	103 A	52	0.02	140	0.0031	first bottle
	103 B	65	0.00	100	0.0003	second bottle

Table A.7. Total Nitrogen Analysis

RUN #	GP94-101	GP94-101 (duplicate)	GP94-108	GP94-108 (duplicate)	GP94-108 (triplicate)	average	
2	0.1146					0.1146	
3	0.1064					0.1064	
4	0.1124					0.1124	
original BLS	**0.1263**	**0.1182**	**0.1052**	**0.1082**	**0.0973**	**0.1110**	
10	0.1044					0.1044	
11	0.097	0.1268				0.1119	*
12	0.0938					0.0938	
13	0.1047					0.1047	
15	0.1013					0.1013	
16	0.1217					0.1217	
17	0.0847					0.0847	
18	0.1025					0.1025	
19	0.1035					0.1035	
20	0.0879					0.0879	
22	0.096	0.1014				0.0987	
23	0.1169	0.1219				0.1194	
24		0.1154				0.1154	
25	0.1303	0.1127				0.1215	*
26	0.1008	0.1029				0.1019	
31	0.1126					0.1126	
32	0.1144	0.1088				0.1116	
33	0.1124	0.1157				0.1141	
34	0.1128	0.1145				0.1137	
35	0.0932					0.0932	
36	0.096	0.1061				0.1011	
39	0.1162	0.1108				0.1135	
40	0.114	0.1152				0.1146	
41	0.0988					0.0988	
42	0.0949	0.1071				0.1010	*
43	0.0966					0.0966	
44	0.089					0.0890	
49	0.1084	0.114				0.1112	
50	0.095	0.1047				0.0999	
51	0.1044	0.1073				0.1059	
53	0.1046	0.0942				0.0994	
54	0.1031	0.1092				0.1062	
55	0.0878					0.0878	
56	0.0984	0.112				0.1052	*
57			0.0888	0.0894		0.0891	

* The difference between the duplicate analysis is greater than 0.01 wt. %.

Table A.7. Total Nitrogen Analysis (continued)

Run #	GP94-101	GP94-101 (duplicate)	GP94-108	GP94-108 (duplicate)	GP94-108 (triplicate)	average	
58			0.0987	0.0951		0.0969	
59			0.0863	0.1078		0.0971	*
60			0.0795	0.1208		0.1002	*
61			0.0796	0.1045		0.0921	*
62			0.065	0.0843		0.0747	*
63			0.0926	0.0874		0.0900	
64			0.113	0.0967		0.1049	*
66			0.1049	0.1042		0.1046	
67			0.1113	0.0921		0.1017	*
68			0.1052	0.0973		0.1013	
70			0.1023	0.1058		0.1041	
71			0.1248			0.1248	
72			0.1069	0.1033		0.1051	
74			0.1147			0.1147	
75			0.1015	0.0977		0.0996	
76			0.1099	0.0946		0.1023	*
77			0.0897	0.0886		0.0892	
78			0.0956	0.0766		0.0861	*
79			0.1005	0.0828		0.0917	*
81			0.0915	0.0684		0.0800	*
82			0.0899	0.0961		0.0930	
83			0.0828	0.1064		0.0946	*
84			0.0966	0.1005		0.0986	
85			0.0972			0.0972	
86			0.0831			0.0831	
87			0.0928	0.097		0.0949	
88			0.086	0.1019		0.0940	*
89			0.0795	0.1085		0.0940	*
90			0.1044	0.108		0.1062	
91			0.1054	0.1195		0.1125	*
92			0.0925	0.1172		0.1049	*
93			0.0977	0.1072		0.1025	
94			0.088	0.1006		0.0943	*
95			0.0801	0.098		0.0891	*
96			0.0933	0.1006		0.0970	
98			0.0869			0.0869	

* The difference between the duplicate analysis is greater than 0.01 wt. %.

Appendix B
Experimental Guidelines

B.1. Equipment Preparation

1. **LEFR reactor set-up. (NOTE: The reactor must be at room temperature.)**

- Position the collector to the desired pathlength. (Cyclone must not be in place)
- Verify that all input gas and cooling water lines are securely connected to the LEFR.
- Turn on cooling water and set the temperature controllers to the desired furnace temperature.

2. **Gas analysis set-up**. Connect all lines according to **Figure** B.1. NOTE: F_1, CO meter and CO_2 meter connections are optional.

- Examine for leaks as they will interfere with all the readings.
- Open both rotameters F_1 and F_2 and adjust the flows so that the bypass flow in the NO-NO_x meter is 1.75 scfh.
- All the gas analyzers need approximately 30 minutes to warm-up. Turn on the NO-NO_x meter pump **only**. (CO and CO_2 meter internal pumps must be off.)
- Place heating tape around the teflon line from the cyclone to the absorption bottles.
- Use water traps where necessary.

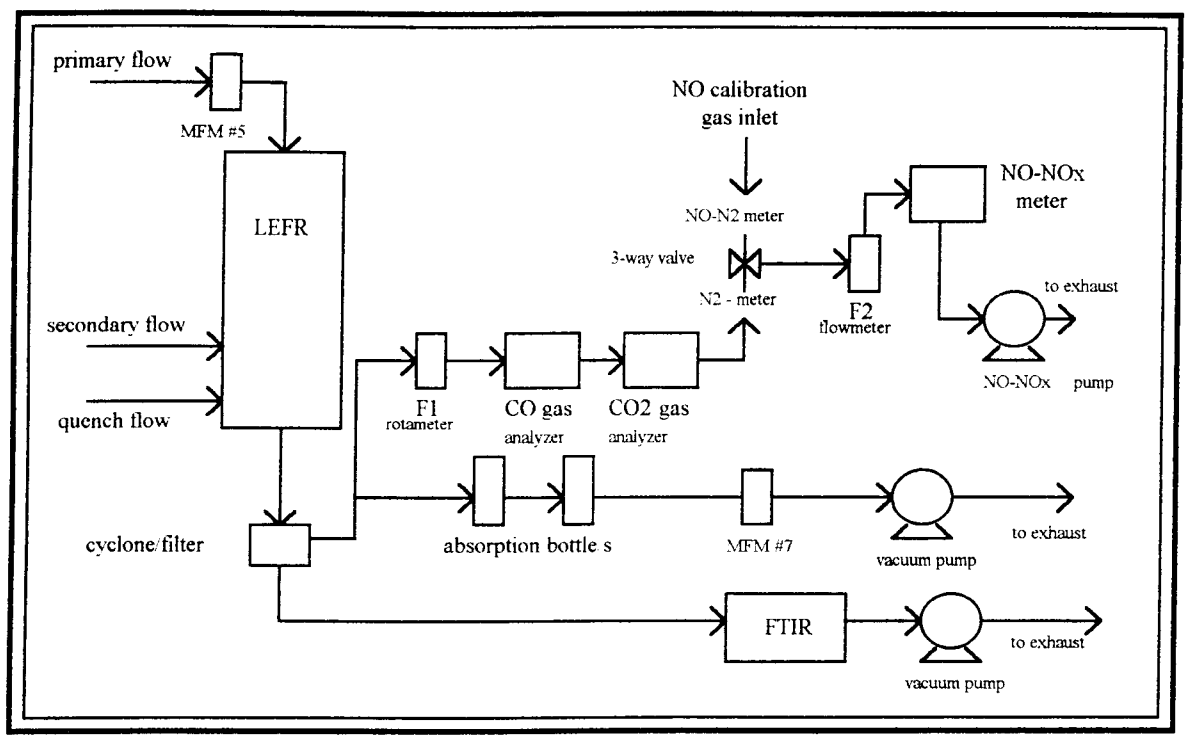


Figure B.1. A Schematic Diagram of the Equipment Set-up

3. **Calibrate the NO-NO_x meter.** NOTE: Use appropriate calibration gas cylinder: NO in N_2 balance or NO in He balance. Check with the data acquisition program for values. (Calibration readings are also checked and recorded after each experiment.)

- Verify that the NO-NO_x meter is completely warmed up.
- Turn 3-way valve to N_2 - meter position. If LEFR secondary and quench gases are not running then ambient air will be pulled into the NO-NO_x meter.
- Set the NO-NO_x meter range to 2.5 and zero the reading by using the **BACKGROUND SUPPRESSION** knob.
- Turn the 3-way valve to NO-N_2 meter position. Set the NO-NO_x meter range to 1000. Let gas run through the NO-NO_x meter at a bypass flow rate of 1.75 scfh and calibrate for NO gas using the **CALIBRATE** knob. Check the display under channel 8 in the data acquisition program. NO levels in ppm (NO_e) can be obtained from the data acquisition voltage readings ($NO_{display}$) by the following formula

$$NO_e = NO_{display} * \text{meter range} / 10 \qquad \text{(B.1)}$$

  where 10 is the maximum voltage output for the full NO/NOx meter range.
- Turn off NO-NO_x source cylinder and turn 3-way valve back to N_2 - meter position. The lines should clear out and the reading must go back to zero.

4. (Optional) **Calibrate the CO and CO_2 gas analyzers**. Refer to their respective operation manuals for the external gas calibration procedures. The CO and CO_2 readings are displayed in the data acquisition program under channels 1 and 2 , respectively.

5. **Check data acquisition for proper set-up**. The following are useful to remember

- When the data acquisition is in the "Analog Display" mode, press "ESC" key to exit. A menu will be shown.
- Set up the data acquisition by following the steps below. Refer to **Table** B.1 for channel assignments.
  - a. Press "C" to go to "set up" mode.
  - b. Choose option 15. Load AUTOBOOT.SET file using option 2 then go back to the main menu. (option 4)
  - c. Choose option 13 for data logging.
    - if the data need not be recorded, set the data logging to the "OFF" position.
    - for the experiments, make sure that the data logging is in the "DISK" position. Option 4 changes the data filename.
    - go back to the main menu (option 10)
  - d. If the feed gas is not N_2 , refer to the mass flow meters' operation manual to determine the appropriate K factors (relative to N_2). Choose option 3 and multiply the scale factors with K.
  - e. Choose option 17 to go back to the normal display mode.
  - f. Option 1 activates the data logging program. This will show the analog display on the screen.

Table B.1. Data Acquisition Set-up

Channel	Type
1	CO gas analyzer
2	CO_2 gas analyzer
3	MFM #3 (Total gas flow)
4	MFM #4 (Total gas flow)
5	MFM #5 (Primary gas flow)
6	MFM #6 (Quench gas flow)
7	MFM #7 (Scrubber gas flow)
8	NO-NO_x meter

B.2. Experiment Procedure

1. **Estimate the gas flows using the equations presented in Section D.2 in Appendix D**. In setting the flows, it is important to turn on the quench flow followed by the total gas flow because the collector body cannot withstand high temperatures. The metering valve is adjusted so that the pressure to MFM #5 is 25 psi. After adjusting the flows, the shut valves for all MFMs are closed.

2. **Assemble the cyclone**. Weigh the fume filters and properly place them in their respective filter holder.

3. **Prepare the absorption bottle.** Fill the absorption bottle with 150 ml of 0.01 M HCl solution.

4. **Set-up the NO-NO_x meter.** Re-zero the NO-NO_x meter. Switch to appropriate range prior to actual run. The range for the NO-NO_x meter is set depending on the gas flows used. The recommended ranges are 0-25 ppm for ν_{tr} < 15 liters/min and 0-10 for ν_{tr} > 15 liters/min. The flow into the NO-NO_x meter must be adjusted to have a bypass flow rate of 1.75 scfh to be consistent with the calibration procedures.

5. **Set-up the black liquor feed.** Fill the test tube about 3/4 full with black liquor particles. Weigh the test tube and load it into the particle feeder.

6. **Turn on the quench gas, total gas and primary gas flows.**

7. **Check for particle flow.** Turn on the motor for the particle feeder to allow the black liquor solids to be entrained by the primary gas flow. The motor speed must be set to low for slower black liquor mass flow rate and longer running time. Wet a piece of towel and place beneath the collector. Immediately after the char particles start

accumulating on the wet towel, turn off the motor for the particle feeder. **Do not shut off any gas flows.**

8. **Attach the cyclone/filter assembly to the bottom of the collector**. Connect all lines leading to desired gas analyzers.

9. **Allow gases to flow into the absorption bottle.** Turn on the pump downstream to the absorption bottles and regulate the flow using MFM #7 to about 4 liters/min. Heat the teflon line to the absorption bottle.

10. **Obtain a FTIR reference gas reading if desired.**

11. **Start the run.** Simultaneously, turn on the motor for the particle feeder and activate the data acquisition program. Check that the primary flow is stable. A decrease of 2-3 ml/min is acceptable. However, when the primary flow starts to decrease continuously, finish the experiment immediately (skip to **step** 13).

12. **Obtain FTIR readings (instantaneous) after 2 minutes of runtime if desired.**

13. **End the experiment.** Simultaneously, shut off the primary flow and place the motor for the particle feeder in the reverse mode to lower the test tube. The total gas flow and the quench flow must be kept flowing into the reactor until the NO level is down to zero.

14. **Shut off the scrubber gas flow, the total gas flow and the quench gas flow.** The scrubber gas flow must not be left open when there is no flow into the LEFR to prevent potential NH_3 loss in air.

15. **Turn off the data acquisition after gathering all pertinent NO data.**

16. **Collect all data.** Weigh the char and the fume particles from the cyclone/filter assembly. As much as possible, weigh the particulates immediately after the experiment to prevent any water absorption from the ambient air. Weigh the test tube containing the black liquor particles. Store the absorption bottle solution for NH_3 analysis.

17. **Flush the feed system.** Place an empty test tube into the particle feeder. Assemble the cyclone. Weigh and place a 9.0 cm polycarbonate filter (filter 3) on the main cyclone outlet. Plug the outlets for filter holders 1 and 2. Attach the cyclone to the bottom of the collector and flush the feed system at maximum primary gas flow rate for at least 1 minute. Use the same quench and total gas flows as in the experiment. Collect and weigh the char and fume particles from this procedure. Do not store particulates.

18. **Flush the injector.** Disconnect the stainless steel tube attached to the injector. Open the quench gas flow to at least 25 liters/min. Plug the collector outlet for at least 20 seconds. This allows the gas to flow into the injector and thus, back-flushing it.

19. **Check the NO calibration**. Allow the NO calibration gas to flow through the NO-NO_x meter. Record the readings into the same data acquisition file as the experiment. NOTE: The bypass rotameter should read 1.75 scfh.

Appendix C
Analytical Procedures

C.1 Orion Ion-Selective Electrode - Ammonia Analysis

1. Prepare the ion-selective electrode (ISE) according to the instruction manual.

- Unscrew top cap and remove the glass electrode from the outer body. Set aside carefully.
- Remove the bottom cap. Smoothly stretch the membrane across the opening and place against the threads. Be careful not to puncture the membrane. Screw the bottom cap on until finger tight.
- Fill the outer body with 2.5 ml diluted internal filling solution (1:10 to improve electrode response).
- Place the glass electrode into the electrode outer body and screw on the top cap.
- Shake the electrode fully to remove air bubbles.

2. Prepare 10 ppm N standard and 1000 ppm N standard solutions by dissolving NH_4Cl crystals in distilled water.

3. Calibrate the electrode.

- In 100 ml of ammonia-free distilled water, add 2 ml of pH-adjusting ionic strength adjuster (ISA) to assure correct pH. Use a 125 ml Erlenmeyer flask to minimize surface-area-to-volume ratio. Add increments of a 10 ppm as N standard according to the table below.

Table C.1. Guidelines for Ammonia Calibration

Step	Pipet Size A - 1 ml or B - 2 ml	Added Volume (mL)	Concentration (ppm N)
0	-	0	0
1	A	0.1	0.01
2	A	0.1	0.02
3	A	0.2	0.04
4	A	0.2	0.06
5	A	0.4	0.10
6	B	2.0	0.30
7	B	2.0	0.49

- Place electrode into the solution. Verify that there are no air bubbles at the electrode tip as they might interfere with the readings.

- Stir solution thoroughly and measure the electrode potential after each increment (from steps 0 to 7). NOTE: Time response is slow at low levels. User must wait about 20-25 minutes for readings to stabilize. The user must be consistent with the starting mV reading for each analysis.
- Soak electrode in a pH 4 buffer solution for at least 5 minutes in between readings .
- Always rinse the electrode with distilled water to prevent contamination between solutions.
- Plot the concentration against the electrode potential Prepare calibration plots daily.

4. Analyze the samples.

- Soak the electrode tip in an ammonia-free pH 4 buffer solution for at least 5 minutes. Stir throughout the procedure.
- Place electrode into the sample solution. Verify that there are no air bubbles at the electrode tip.
- Stir sample solution thoroughly and measure the electrode potential. Use the calibration plot to determine the NH_3 (in ppm N as NH_3). The amount of NH_3 in milligrams ($NH_{3\,total}$) is given by

$$NH_{3total} = ppm\ N\left(\frac{17\ g\ NH_3}{14\ g\ N}\right)\frac{V_{Stotal}}{1000} \qquad (C.1.1)$$

where *ppm* N is the equivalent concentration obtained from the calibration plot, V_{Stotal} is the volume of the HCl scrubber solution in ml, and 1000 is a conversion factor.

- Always rinse the electrode with distilled water to prevent contamination between solutions.

5. After using the electrode, soak the electrode tip in 1000 ppm as N standard and store.

C.2 Data Acquisition File Analysis

NOTE: The data acquisition file is generated by recording time averaged readings from the mass flow meters and the gas analyzers approximately every 2 seconds. Refer to **Table** B.1 for channel assignments.

1. **Total running time.** The data acquisition file records the date, hour, minute, second and 1/100 second of each reading based on the internal clock. The corresponding time in seconds are calculated as follows

$$t_i = (ta_i - ta_0)* 3600 + (tb_i - tb_0) * 60 + (tc_i - tc_0) + (td_i - td_0)/100 \qquad (C.2.1)$$

where t_a = hour reading
t_b = minute reading
t_c = second reading
t_d = hundredth of a second
o = subscript indicates reading at initial time, t = 0.
i = subscript indicates i^{th} reading
t_i = time at i^{th} reading

The running time, t_{run}, is the time at which the primary flow is turned off (in the case of good runs) or the time at which the primary flow starts to decrease rapidly (in the case of plugging)

2. Primary, total, and quench gas flows are averaged for the total running time or until plugging is evident, whichever is less. NOTE: total gas flow rate = primary gas flow + secondary gas flow.

3. Voltage readings for NO are converted according to **eqn.** B.1 in **Appendix B** to units of ppm.

$$NO_e = NO_{display} * \text{meter range} / 10 \qquad (B.1)$$

where $NO_{display}$ = data acquisition voltage reading for NO, Volts
NO_e = NO concentration, ppm
meter range = NO-NO_x range, ppm

and 10 is a conversion factor. Each NO reading is corrected to its actual value based on NO calibration.

$$NO_i = [NO_{calib}/(NO_r - NO_0)] (NO_{ei} - NO_0) \qquad (C.2.2)$$

where NO_{ei} = NO concentration reading at i^{th} time step, ppm
NO_{calib} = calibration gas concentration, ppm
NO_r = average concentration reading for NO calibration gas, ppm
NO_0 = NO concentration reading at zero NO, ppm
NO_i = actual NO concentration at i^{th} time step, ppm

4. The average for NO levels is calculated along the time at which readings were fairly stable (as indicated by plots generated from Cricket Graph). The following formula applies

$$NO_{mean} = \frac{\Sigma_i([(NO_i + NO_{i+1})/2] * [(t_i + t_{i+1})/2])}{\Sigma_i [(t_i + t_{i+1})/2]) } \qquad (C.2.3)$$

where t_i = time at i^{th} step, seconds

(Repeat for CO and CO_2 readings if needed.) This method may be inaccurate due to fluctuations in the readings. A more appropriate method is to determine the total NO, NO_{total}, from each experiment. The units of NO_{total} are ppm·sec.

$$NO_{total} = \Sigma_i \left([(NO_i + NO_{i+1}) / 2] * [(t_{i+1} - t_i) / 2] \right) \quad \text{(C.2.4)}$$

5. Determine the total scrubber gas flow, $V_{scrubber}$, in liters by applying the trapezoidal rule to obtain area of flow rate vs. time curve

$$V_{scrubber} = \Sigma_i \left([(v_{sr_i} + v_{sr_{i+1}}) / 2] * [(t_{i+1} - t_i) / 2] \right) \quad \text{(C.2.5)}$$

where v_{sr_i} = volumetric flow rate of the gas into the scrubber at i^{th} time step, l/min

Appendix D
Nitrogen Devolatilization Analysis

D.1 Equations

Relevant equations used in the calculations are listed below. Refer to **Figure** D.1 below.

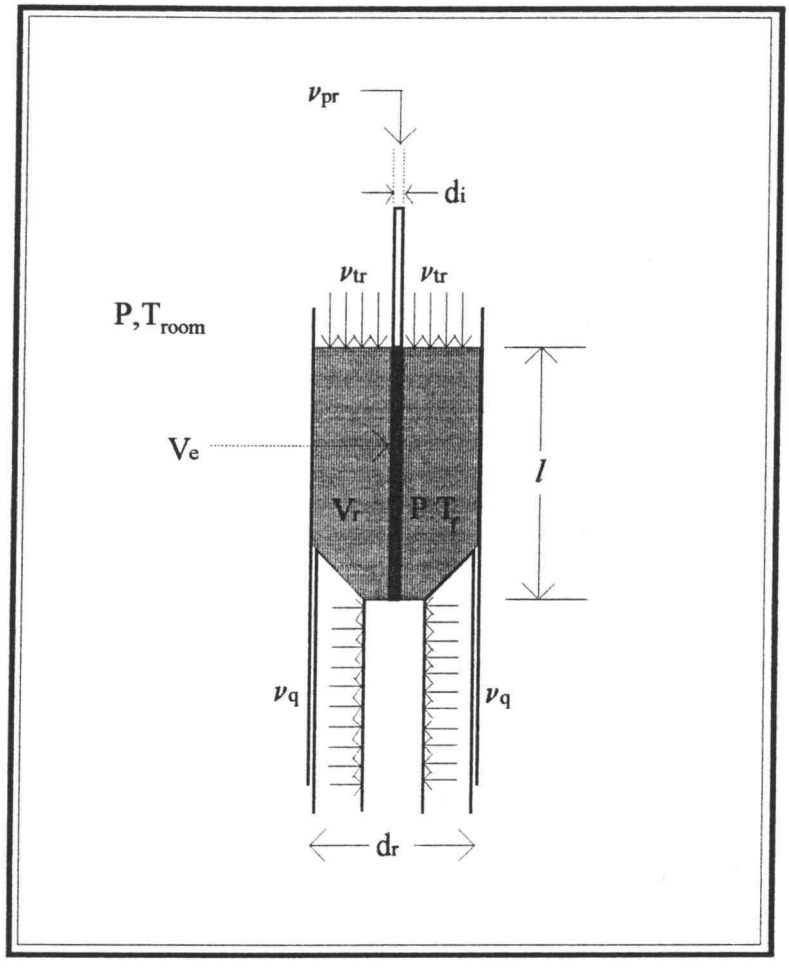


Figure D.1. Reactor Parameters

1. The effective reactor volume, assuming that there are no diffusion or expansion effects, is given by

$$V_e = \pi/4 \; d_i^2 \, l \qquad \text{(D.1)}$$

where V_e = effective reactor volume, cm^3
d_i = inside diameter of the injector (0.344 cm for the old injector; 0.655 cm for the new injector)
l = reactor pathlength, in.

Appropriate conversion factors are required.

2. The total reactor volume is given by

$$V_r = \pi/4 \; d_r^2 \, l \qquad \text{(D.2)}$$

where V_r = total reactor volume, cm^3
d_r = inside diameter of the reactor; 7 cm
l = reactor pathlength, in.

Appropriate conversion factors are required.

3. The gas flow rate into the reactor is corrected to the appropriate flow rate at the furnace temperature by the ideal gas relation

$$\nu_{pf} = \nu_{pr} \frac{T_f}{T_{room}} \qquad \text{(D.3)}$$

and

$$\nu_{tf} = \nu_{tr} \frac{T_f}{T_{room}} \qquad \text{(D.4)}$$

where ν_{pf} = primary flow rate at furnace temperature, l/min
ν_{pr} = primary flow rate at room temperature, l/min
ν_{tf} = total flow rate at furnace temperature, l/min
ν_{tr} = total flow rate at room temperature, l/min
T_{room} = room temperature, K
T_f = furnace temperature, K

4. The velocity of the primary gas exiting the injector, u_i, is given by

$$u_i = \nu_{pf} / (\pi/4 \, d_i^2) \qquad \text{(D.5)}$$

5. The velocity of total gas, u_t, entering the reactor

$$u_t = \nu_{tf} / (\pi/4 \, d_i^2) \qquad \text{(D.6)}$$

6. The residence time in seconds can be estimated by

$$\tau_p = \frac{V_e}{\nu_{pf}} \tag{D.7}$$

or

$$\pi = \frac{V_r}{\nu_{tf}} \tag{D.8}$$

A 1:1 velocity ratio of primary gas to total gas flow ($u_i = u_t$) must be maintained for $\tau_p = \pi$. If $\tau_p \neq \pi$ then, the residence time is taken as the average

$$\tau_{ave} = \tfrac{1}{2}(\tau_p + \pi) \tag{D.9}$$

Appropriate conversion factors are required.

7. The amount of initial fuel nitrogen in the black liquor that formed NO is given by

$$\frac{\text{g N as NO}}{\text{g fuel N}} = \frac{\left(\frac{NO_{mean}}{10^6}\right)\left(\frac{P(\nu_t + \nu_q)(t_{run})}{RT_{room}}\right)\left(14\frac{\text{g N}}{\text{mol NO}}\right)}{N_{in}} \tag{D.10}$$

or if the NO_{total} is given

$$\frac{\text{g N as NO}}{\text{g fuel N}} = \frac{\left(\frac{NO_{total}}{10^6}\right)\left(\frac{P(\nu_t + \nu_q)}{R\,T_{room}}\right)\left(14\frac{\text{g N}}{\text{mol NO}}\right)}{N_{in}} \tag{D.11}$$

where

NO_{mean}	=	average NO concentration, ppm
NO_{total}	=	total NO detected by the NO-NO_x meter, ppm·sec
ν_{qr}	=	quench gas flow rate at room temperature, l/min
t_{run}	=	total running time, min
N_{in}	=	total fuel nitrogen in the black liquor, g
P	=	reactor pressure; 1 atm
R	=	gas constant; 0.08205 $\frac{\text{li atm}}{\text{mol K}}$

8. The amount of fuel nitrogen that formed NH_3 is given by

$$\frac{\text{g N as NH}_3}{\text{g fuel N}} = \frac{\left(\frac{NH_{3\,total}}{1000\,^{mg}/_{g}}\right)\left(\frac{(\nu_t + \nu_q)t_{run}}{V_{scrubber}}\right)\left(\frac{14\text{g N}}{17\text{g NH}_3}\right)}{N_{in}} \tag{D.12}$$

where $NH_{3\,total}$ = total NH_3 absorbed in the HCl solution, mg
$V_{scrubber}$ = total gas flow into the HCl solution, l

9. The percentage of input fuel nitrogen that is converted to char-N (N_{char}) is given by

$$\frac{g\ N_{char}}{g\ fuel\ N} = (wt\ \%\ N_{char})\ (char_{ex}) / (N_{in}) \qquad (D.13)$$

where wt. % N_{char} = weight percent of char-N from total nitrogen analysis
$char_{ex}$ = amount of char obtained during the experiments, g

D.2 Estimating Gas Flow Rates

The gas flow rates at room temperature can be estimated by allowing $\tau_p = \tau$ and back-calculating using **eqns.** D.3, D.4, D.7 and D.8. Thus, the relationship between the primary and secondary gas flow rates at room temperature is

$$v_{pr} = v_{tr} \frac{V_e}{V_r} \qquad (D.14)$$

where

$$v_{tr} = \left(\frac{T_{room}}{T_f}\right)\left(\frac{V_r}{\tau_t}\right) \qquad (D.15)$$

The quench gas flow rate at the tip of the collector is equal to v_{tr}. This accounted for 75 % of the total quench gas flow.

D.3 Summarized Results

Tables D.1, D.2 D.3, D.4, and D.5 were generated to provide a summarized overview of the results. They include operating conditions, data acquisition file analysis, pertinent weight data, ammonia analysis absorption analysis, and total nitrogen analysis.

The operating conditions and pertinent weight data were taken from the raw data in **Appendix A**. The data acquisition file analysis and ammonia absorption analysis were obtained using the procedures outlined in **Appendix C**. The total nitrogen analysis reported for the char were results to the analysis performed at the Oregon State University Plant Analysis Lab in Department of Soil Science.

Table D.1. Feasibility Studies in the LEFR

EXPERIMENT #	***10***	***11***	***12***	***13***	***15***	***2***
TEMPERATURE (C)	***700***	***700***	***800***	***800***	***800***	***900***
ROOM TEMPERATURE (C)	22.6	22.6	21.2	20.9	22.4	19.5
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 10**	**PPY 11**	**PPY 12**	**PPY 13**	**PPY 15**	**PPY 2**
v_{pr} (l/min)	0.096	0.101	0.100	0.099	0.105	0.105
v_{tr} (l/min)	12.93	12.87	12.92	12.86	12.87	12.74
v_{qr} (l/min)	20.06	19.70	20.20	20.00	20.45	19.94
v_{sr} (l/min)	3.95	3.89	4.24	4.09	4.05	4.07
$V_{scrubber}$ (l)	20.06	19.41	19.07	12.38	16.10	20.77
RUNNING TIME (sec)	240.35	298.86	269.96	181.75	238.87	306.16
time at plug					189.93	
filter flow time	240.35	298.86	269.96	181.75	238.87	306.16
RESIDENCE TIME						
l (inches)	17	17	17	17	17	17
Ve (cm3)	3.78	3.78	3.78	3.78	3.78	3.78
Vr (cm3)	1661.77	1661.77	1661.77	1661.77	1661.77	1661.77
u_i (cm/min)	3.62	3.80	4.18	4.12	4.36	4.81
u_t (cm/min)	1.11	1.10	1.22	1.22	1.21	1.33
τ_p (sec)	0.72	0.68	0.62	0.63	0.59	0.54
τ_t (sec)	2.34	2.36	2.12	2.12	2.13	1.95
τ_{ave} **(sec)**	**1.53**	**1.52**	**1.37**	**1.38**	**1.36**	**1.25**
NO mean (ppm)	-	-	-	-	-	5.6847
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-	-	21.96%
NO total (ppm)	6.2057	7.4563	-	8.7836	5.5124	-
g N as NO/ g fuel N (eqn. D.11)	**5.91%**	**5.69%**	-	**14.04%**	**9.61%**	-
Weight Data						
BL feed weight (g)	1.8021	2.2198	1.8378	1.0746	0.9945	2.2668
fuel N (g)	**0.0020**	**0.0025**	**0.0020**	**0.0012**	**0.0011**	**0.0025**
mass flowrate (g/min)	0.4499	0.4457	0.4085	0.3548	0.3142	0.4442
char weight (g)	1.1629	1.4199	1.0153	0.6817	0.5659	1.2219
char yield	64.53%	63.97%	55.25%	63.44%	56.90%	53.90%
Ammonia absorption						
NH3 in solution (mg)	0.0040	0.0045	0.0120	0.0060	0.0038	0.0186
g N as NH3/ g fuel N	**1.09%**	**1.27%**	**3.77%**	**3.33%**	**2.31%**	**4.88%**
Total Nitrogen Analysis						
% weight char-N	**0.1044%**	**0.0970%**	**0.0938%**	**0.1047%**	**0.1013%**	**0.1146%**
char-N (g)	0.00121	0.00138	0.00095	0.00071	0.00057	0.00140
g char-N/ g fuel N	**60.69%**	**55.90%**	**46.68%**	**59.84%**	**51.93%**	**55.65%**

Table D.1. Feasibility Studies in the LEFR (continued)

EXPERIMENT #	***3***	***4***	***16***	***17***	***18***	***19***
TEMPERATURE (C)	***900***	***900***	***1000***	***1000***	***1100***	***850***
ROOM TEMPERATURE (C)	19.5	19.5	22.4	20.4	23.2	22.8
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 3**	**PPY 4**	**PPY 16**	**PPY 17**	**PPY 18**	**PPY 19**
v_{pr} (l/min)	0.107	0.105	0.105	0.105	0.101	0.098
v_{tr} (l/min)	12.97	12.92	12.86	13.02	12.97	12.97
v_{qr} (l/min)	20.01	20.21	20.38	20.08	19.93	20.11
v_{sr} (l/min)	3.10	3.98	4.04	4.02	4.09	3.93
$V_{scrubber}$ (l)	18.33	19.78	20.62	20.34	16.22	19.66
RUNNING TIME (sec)	354.87	298.19	306.15	303.46	237.67	300.16
time at plug						196.03
filter flow time	354.87	298.19	306.15	303.46	237.67	300.16
RESIDENCE TIME						
l (inches)	17	17	17	17	17	17
Ve (cm3)	3.78	3.78	3.78	3.78	3.78	3.78
V_r (cm3)	1661.77	1661.77	1661.77	1661.77	1661.77	1661.77
u_i (cm/min)	4.91	4.82	5.17	5.21	5.32	4.26
u_t (cm/min)	1.35	1.35	1.44	1.47	1.56	1.28
τ_p (sec)	0.53	0.54	0.50	0.50	0.49	0.61
τ_t (sec)	1.92	1.93	1.80	1.77	1.66	2.03
τ_{ave} **(sec)**	**1.22**	**1.23**	**1.15**	**1.13**	**1.07**	**1.32**
NO mean (ppm)	6.6397	6.1140	3.2272	5.3894	-	-
g N as NO/ g fuel N (eqn. D.10)	26.83%	22.47%	16.69%	22.65%	-	-
NO total (ppm)	-	-	11.2174	20.8084	5.5931	7.1866
g N as NO/ g fuel N (eqn. D.11)	-	-	**11.37%**	**17.29%**	**7.44%**	**12.29%**
Weight Data						
BL feed weight (g)	2.5355	2.3534	1.7062	2.0857	1.2825	1.0052
fuel N (g)	**0.0028**	**0.0026**	**0.0019**	**0.0023**	**0.0020**	**0.0011**
mass flowrate (g/min)	0.4287	0.4735	0.3433	0.4088	0.3559	0.3077
char weight (g)	1.5212	1.179	0.932	1.1863	0.9491	0.4156
char yield	60.00%	50.10%	54.62%	56.88%	74%	41.35%
Ammonia absorption						
NH3 in solution (mg)	0.0130	0.0160	0.0066	0.0111	0.0033	0.0043
g N as NH_3/ g fuel N	**4.04%**	**4.21%**	**2.38%**	**3.25%**	**1.53%**	**2.66%**
Total Nitrogen Analysis						
% weight char-N	**0.1064%**	**0.1124%**	**0.1217%**	**0.0847%**	**0.1025%**	**0.1035%**
char-N (g)	0.00162	0.00133	0.00113	0.00100	0.00097	0.00043
g char-N/ g fuel N	**57.51%**	**50.73%**	**59.89%**	**43.40%**	**68.34%**	**38.55%**

Table D.1. Feasibility Studies in the LEFR (continued)

EXPERIMENT #	***20***	***21***	***22***	***23***	***24***	***25***
TEMPERATURE (C)	***850***	***900***	***900***	***900***	***1100***	***1100***
ROOM TEMPERATURE (C)	22.6	23.5	23.5	23.5	20.2	20.2
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 20**	**PPY 21**	**PPY 22**	**PPY 23**	**PPY 24**	**PPY 25**
v_{pr} (l/min)	0.099	0.099	0.101	0.102	0.099	0.101
v_{tr} (l/min)	13.05	12.75	12.77	12.93	12.96	12.90
v_{qr} (l/min)	20.07	19.94	20.14	19.82	20.52	20.08
v_{sr} (l/min)	3.92	3.86	-	3.88	3.83	3.85
$V_{scrubber}$ (l)	19.55	19.21	-	19.26	19.11	19.17
RUNNING TIME (sec)	299.29	298.85	300.06	297.75	299.46	298.41
time at plug	157.25	74.65	-	-	-	286.27
filter flow time	330.99	298.85	-	297.75	299.46	298.41
RESIDENCE TIME						
l (inches)	17	17	17	17	17	17
V_e (cm3)	3.78	3.78	3.78	3.78	3.78	3.78
V_r (cm3)	1661.77	1661.77	1661.77	1661.77	1661.77	1661.77
u_i (cm/min)	4.28	4.47	4.57	4.59	5.27	5.38
u_t (cm/min)	1.29	1.31	1.31	1.33	1.58	1.57
τ_p (sec)	0.61	0.58	0.57	0.56	0.49	0.48
τ_t (sec)	2.01	1.98	1.97	1.95	1.64	1.65
τ_{ave} **(sec)**	**1.31**	**1.28**	**1.27**	**1.26**	**1.07**	**1.07**
NO mean (ppm)	-	-	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-	-	-
NO total (ppm)	7.8678	2.0995	16.6113	20.2247	0.8928	1.0674
g N as NO/ g fuel N (eqn. D.11)	**13.64%**	**10.42%**	**14.03%**	**14.93%**	**0.83%**	**0.92%**
Weight Data						
BL feed weight (g)	0.9932	0.3413	2.0186	2.2991	1.8937	1.9987
fuel N (g)	**0.0011**	**0.0004**	**0.0022**	**0.0026**	**0.0021**	**0.0022**
mass flowrate (g/min)	0.3790	0.2743	0.4053	0.4597	0.3816	0.4189
char weight (g)	0.4166	0.1341	0.8158	1.0374	0.6257	0.7109
char yield	41.95%	39.29%	40.41%	45.12%	33.04%	35.57%
Ammonia absorption						
NH3 in solution (mg)	0.0043	0.0033	-	0.0060	0.0040	0.0506
g N as NH3/ g fuel N	**2.70%**	**6.16%**		**1.65%**	**1.36%**	**16.09%**
Total Nitrogen Analysis						
% weight char-N	**0.0879%**	-	**0.0960%**	**0.1169%**	**0.1154%**	**0.1215%**
char-N (g)	0.00037	-	0.00078	0.00121	0.00072	0.00086
g char-N/ g fuel N	**33.22%**	-	**34.95%**	**47.52%**	**34.35%**	**38.93%**

Table D.2. Nitrogen Evolution at 2 seconds residence time in the LEFR

EXPERIMENT #	***55***	***57***	***58***	***59***	***60***	***64***
TEMPERATURE (C)	***900***	***700***	***700***	***800***	***800***	***900***
ROOM TEMPERATURE (C)	27	29.2	30.8	31.1	29.9	29.8
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 55**	**PPY 57**	**PPY 58**	**PPY 59**	**PPY 60**	**PPY 64**
v_{pr} (l/min)	0.087	0.106	0.108	0.098	0.099	0.114
v_{tr} (l/min)	10.36	12.57	12.54	11.31	11.53	13.31
v_{qr} (l/min)	13.92	16.83	16.71	15.12	15.27	17.29
v_{sr} (l/min)	3.93	3.62	3.87	3.92	3.97	4.82
$V_{scrubber}$ (l)	10.11	18.26	12.72	19.46	9.77	11.09
RUNNING TIME (sec)	154.12	300.22	196.96	297.64	147.75	166.32
time at plug	109.79	-	180.98	-	109.69	144.18
filter flow time	154.12	300.22	196.96	297.64	147.75	137.97
RESIDENCE TIME						
l (inches)	14	14	14	14	14	18
V_e (cm3)	11.87	11.87	11.87	11.87	11.87	15.26
V_r (cm3)	1368.51	1368.51	1368.51	1368.51	1368.51	1759.52
u_i (cm/min)	1.02	1.02	1.03	1.04	1.05	1.32
u_t (cm/min)	1.05	1.05	1.04	1.04	1.06	1.34
τ_p (sec)	2.09	2.10	2.06	2.06	2.04	2.08
τ (sec)	2.03	2.03	2.05	2.06	2.01	2.05
τ_{ave} **(sec)**	**2.06**	**2.06**	**2.05**	**2.06**	**2.02**	**2.06**
NO mean (ppm)	-	4.1025	-	-	-	4.0884
g N as NO/ g fuel N (eqn. D.10)	-	15.19%	-	-	-	15.84%
NO total (ppm)	5.9283	16.2770	8.4163	31.3061	7.7950	6.7207
g N as NO/ g fuel N (eqn. D.11)	**13.35%**	**12.04%**	**10.55%**	**19.59%**	**15.28%**	**10.83%**
Weight Data						
BL feed weight (g)	0.5522	2.0207	1.1807	2.1337	0.6935	0.9631
fuel N (g)	**0.0006**	**0.0022**	**0.0013**	**0.0024**	**0.0008**	**0.0011**
mass flowrate (g/min)	0.3018	0.4038	0.3914	0.4301	0.3793	0.4008
char weight (g)	0.304	1.4635	0.7334	1.2951	0.379	0.5277
char yield	55.05%	72.43%	62.12%	60.70%	54.65%	54.79%
Ammonia absorption						
NH3 in solution (mg)	0.0032	0.0040	0.0037	0.0091	0.0041	0.0028
g N as NH3/ g fuel N	**2.69%**	**1.18%**	**1.77%**	**2.12%**	**2.95%**	**1.66%**
Total Nitrogen Analysis						
% weight char-N	0.0878%	0.0891%	0.0969%	0.0971%	0.1002%	0.1049%
char-N (g)	0.00027	0.00130	0.00071	0.00126	0.00038	0.00055
g char-N/ g fuel N	**43.55%**	**58.14%**	**54.23%**	**53.10%**	**49.33%**	**51.78%**

Table D.2. Nitrogen Evolution at 2 seconds residence time in the LEFR (continued)

EXPERIMENT #	***67***	***68***	***70***	***71***	***72***	***74***
TEMPERATURE (C)	***1000***	***1000***	***1000***	***1100***	***1100***	***1100***
ROOM TEMPERATURE (C)	26.2	28.2	28.2	28	27.1	27.1
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 67**	**PPY 68**	**PPY 70**	**PPY 71**	**PPY 72**	**PPY 74**
v_{pr} (l/min)	0.107	0.106	0.101	0.097	0.098	0.097
v_{tr} (l/min)	12.44	12.31	12.39	11.40	11.35	11.38
v_{qr} (l/min)	16.46	16.41	16.49	15.17	15.33	15.27
v_{sr} (l/min)	4.78	3.99	4.91	4.91	4.63	4.77
$V_{scrubber}$ (l)	16.06	6.49	29.31	10.86	21.62	10.53
RUNNING TIME (sec)	201.63	214.82	359.7	132.81	298.47	136.71
time at plug	179.55	191.15	-	103.04	246.62	126.82
filter flow time	201.63	106.01	359.7	132.81	282.26	134.24
RESIDENCE TIME						
l (inches)	18	18	18	18	18	18
Ve (cm3)	15.26	15.26	15.26	15.26	15.26	15.26
Vr (cm3)	1759.52	1759.52	1759.52	1759.52	1759.52	1759.52
u_i (cm/min)	1.37	1.34	1.28	1.33	1.34	1.33
u_t (cm/min)	1.37	1.35	1.36	1.35	1.35	1.35
τ_p (sec)	2.01	2.04	2.14	2.07	2.05	2.06
τ (sec)	2.00	2.03	2.02	2.03	2.03	2.03
τ_{ave} **(sec)**	**2.00**	**2.04**	**2.08**	**2.05**	**2.04**	**2.05**
NO mean (ppm)	-	-	1.1796	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	3.73%	-	-	-
NO total (ppm)	1.8105	3.0775	5.8806	0.0895	0.3405	0.4434
g N as NO/ g fuel N (eqn. D.11)	**2.50%**	**3.62%**	**3.10%**	**0.22%**	**0.27%**	**0.67%**
Weight Data						
BL feed weight (g)	1.0752	1.2468	2.7935	0.5559	1.7108	0.9088
fuel N (g)	**0.0012**	**0.0014**	**0.0031**	**0.0006**	**0.0019**	**0.0010**
mass flowrate (g/min)	0.3593	0.3914	0.4660	0.3237	0.4162	0.4300
char weight (g)	0.5117	0.6212	1.4451	0.177	0.5758	0.307
char yield	47.59%	49.82%	51.73%	31.84%	33.66%	33.78%
Ammonia absorption						
NH3 in solution (mg)	0.0028	0.0021	0.0096	0.0081	0.0067	0.0025
g N as NH3/ g fuel N	**1.18%**	**1.94%**	**1.50%**	**5.87%**	**1.77%**	**1.19%**
Total Nitrogen Analysis						
% weight char-N	0.1017%	0.1013%	0.1041%	0.1248%	0.1051%	0.1147%
char-N (g)	0.00052	0.00063	0.00150	0.00022	0.00061	0.00035
g char-N/ g fuel N	**43.60%**	**45.47%**	**48.52%**	**35.80%**	**31.87%**	**34.91%**

Table D.2. Nitrogen Evolution at 2 seconds residence time in the LEFR (continued)

EXPERIMENT #	***75***	***76***	***77***	***78***	***79***	***90***
TEMPERATURE (C)	***900***	***850***	***800***	***750***	***700***	***600***
ROOM TEMPERATURE (C)	25.5	23.9	23.5	23.4	23.3	27
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 75**	**PPY 76**	**PPY 77**	**PPY 78**	**PPY79**	**PPY 90**
v_{pr} (l/min)	0.101	0.107	0.112	0.119	0.124	0.105
v_{tr} (l/min)	11.88	12.47	13.01	13.60	14.30	11.97
v_{qr} (l/min)	16.02	16.54	17.25	18.11	19.03	15.85
v_{sr} (l/min)	4.95	4.95	4.93	4.97	4.96	4.97
$V_{scrubber}$ (l)	24.51	25.26	25.14	23.13	24.81	24.68
RUNNING TIME (sec)	299.18	306.38	306.1	253.37	297.81	297.97
time at plug	280.89	-	-	248.87	-	-
filter flow time	299.18	306.38	306.1	253.37	297.81	297.97
RESIDENCE TIME						
l (inches)	16	16	16	16	16	12
Ve (cm3)	13.57	13.57	13.57	13.57	13.57	10.18
Vr (cm3)	1564.01	1564.01	1564.01	1564.01	1564.01	1173.01
u_i (cm/min)	1.19	1.21	1.21	1.23	1.22	0.91
u_t (cm/min)	1.21	1.22	1.22	1.22	1.22	0.90
τ_p (sec)	2.04	2.02	2.02	1.98	2.00	2.01
τ (sec)	2.01	1.99	1.99	2.00	2.00	2.02
τ_{ave} **(sec)**	**2.03**	**2.01**	**2.01**	**1.99**	**2.00**	**2.01**
NO mean (ppm)	3.8667	5.2768	5.5962	-	2.7555	0.6790
g N as NO/ g fuel N (eqn. D.10)	14.11%	20.08%	20.15%	-	11.36%	2.28%
NO total (ppm)	15.4604	22.9148	25.4098	14.4671	12.1064	3.0100
g N as NO/ g fuel N (eqn. D.11)	**12.05%**	**17.07%**	**17.93%**	**13.96%**	**10.05%**	**2.04%**
Weight Data						
BL feed weight (g)	1.8419	2.0146	2.2216	1.7033	2.0817	2.1034
fuel N (g)	**0.0020**	**0.0022**	**0.0025**	**0.0019**	**0.0023**	**0.0023**
mass flowrate (g/min)	0.3934	0.3945	0.4355	0.4106	0.4194	0.4235
char weight (g)	0.9759	1.1286	1.2175	0.9285	1.1872	1.4655
char yield	52.98%	56.02%	54.80%	54.51%	57.03%	69.67%
Ammonia absorption						
NH3 in solution (mg)	0.0043	0.0056	0.0037	0.0060	0.0037	0.0080
g N as NH3/ g fuel N	**0.98%**	**1.22%**	**0.76%**	**1.51%**	**0.88%**	**1.58%**
Total Nitrogen Analysis						
% weight char-N	0.0996%	0.1023%	0.0892%	0.0861%	0.0917%	0.1062%
char-N (g)	0.00097	0.00115	0.00109	0.00080	0.00109	0.00156
g char-N/ g fuel N	**47.54%**	**51.63%**	**44.04%**	**42.28%**	**47.11%**	**66.66%**

Table D.2. Nitrogen Evolution at 2 seconds residence time in the LEFR (continued)

EXPERIMENT #	***91***	***92***
TEMPERATURE (C)	***600***	***500***
ROOM TEMPERATURE (C)	29	30.1
FEED GAS	N2	N2
PARTICLE SIZE (um)	90-125	90-125
Data Acquisition File	**PPY 91**	**PPY 92**
v_{pr} (l/min)	0.102	0.117
v_{tr} (l/min)	11.88	13.52
v_{qr} (l/min)	16.05	17.99
v_{sr} (l/min)	4.94	4.88
$V_{scrubber}$ (l)	12.99	19.95
RUNNING TIME (sec)	157.8	244.42
time at plug	128.09	238.32
filter flow time	157.8	242.01
RESIDENCE TIME		
l (inches)	12	12
Ve (cm3)	10.18	10.18
Vr (cm3)	1173.01	1173.01
u_i (cm/min)	0.89	0.90
u_t (cm/min)	0.89	0.90
τ_p (sec)	2.06	2.04
τ (sec)	2.05	2.04
τ_{ave} (sec)	**2.06**	**2.04**
NO mean (ppm)	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-
NO total (ppm)	1.1054	-
g N as NO/ g fuel N (eqn. D.11)	**2.06%**	-
Weight Data		
BL feed weight (g)	0.7630	1.6420
fuel N (g)	**0.0008**	**0.0018**
mass flowrate (g/min)	0.3574	0.4134
char weight (g)	0.4541	1.1419
char yield	59.52%	69.54%
Ammonia absorption		
NH3 in solution (mg)	0.0021	0.0037
g N as NH3/ g fuel N	**1.14%**	**1.07%**
Total Nitrogen Analysis		
% weight char-N	0.1125%	0.1049%
char-N (g)	0.00051	0.00120
g char-N/ g fuel N	**60.32%**	**65.72%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR

EXPERIMENT #	*26*	*31*	*32*	*33*	*34*	*35*
RESIDENCE TIME	***0.85***	***0.65***	***0.85***	***1***	***1.25***	***1.5***
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	20	26.3	26.3	26.3	26.3	26.3
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 26**	**PPY 31**	**PPY 32**	**PPY 33**	**PPY 34**	**PPY 35**
v_{pr} (l/min)	0.152	0.199	0.151	0.121	0.101	0.086
v_{tr} (l/min)	17.57	22.97	17.34	13.99	11.75	10.03
v_{qr} (l/min)	23.53	30.87	23.24	18.74	15.40	13.27
v_{sr} (l/min)	3.92	3.90	3.86	3.89	3.88	3.83
$V_{scrubber}$ (l)	23.59	11.94	23.09	23.21	19.26	22.10
RUNNING TIME (sec)	360.7	183.62	359.22	358.39	297.7	346.03
time at plug	-	125.84	275.51	342.41	236.7	115.62
filter flow time	360.7	183.62	359.22	358.39	297.7	346.03
RESIDENCE TIME						
l (inches)	10	10	10	10	10	10
Ve (cm3)	8.48	8.48	8.48	8.48	8.48	8.48
Vr (cm3)	977.51	977.51	977.51	977.51	977.51	977.51
u_i (cm/min)	1.83	2.34	1.77	1.42	1.18	1.01
u_t (cm/min)	1.83	2.34	1.77	1.42	1.20	1.02
τ_p (sec)	0.84	0.65	0.86	1.08	1.29	1.51
τ (sec)	0.83	0.65	0.86	1.07	1.27	1.49
τ_{ave} (sec)	**0.83**	**0.65**	**0.86**	**1.07**	**1.28**	**1.50**
NO mean (ppm)	-	-	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-	-	-
NO total (ppm)	14.1764	2.4735	12.4835	29.6182	15.2531	7.7700
g N as NO/ g fuel N (eqn. D.11)	**12.28%**	**7.35%**	**13.42%**	**18.66%**	**14.80%**	**14.66%**
Weight Data						
BL feed weight (g)	2.488	0.9298	1.9384	2.6667	1.4366	0.6336
fuel N (g)	**0.0028**	**0.0010**	**0.0022**	**0.0030**	**0.0016**	**0.0007**
mass flowrate (g/min)	0.4139	0.4433	0.4221	0.4673	0.3642	0.3288
char weight (g)	1.0509	0.378	0.9179	1.4759	0.5191	0.2905
char yield	42.24%	40.65%	47.35%	55.35%	36.13%	45.85%
Ammonia absorption						
NH3 in solution (mg)	0.0003	0.0000	0.0052	0.0089	0.0045	0.0005
g N as NH_3/ g fuel N	**0.11%**	**0.00%**	**2.10%**	**2.09%**	**1.63%**	**0.38%**
Total Nitrogen Analysis						
% weight char-N	**0.1019%**	**0.1126%**	**0.1116%**	**0.1141%**	**0.1137%**	**0.0932%**
char-N (g)	0.00107	0.00043	0.00102	0.00168	0.00059	0.00027
g char-N/ g fuel N	**38.78%**	**41.24%**	**47.61%**	**56.89%**	**37.01%**	**38.50%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	***36***	***39***	***40***	***41***	***42***	***43***
RESIDENCE TIME	***1.75***	***1***	***0.65***	***0.85***	***1.25***	***1.5***
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	26.3	26.4	26.4	25.4	25.4	25.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 36**	**PPY 39**	**PPY 40**	**PPY 41**	**PPY 42**	**PPY 43**
v_{pr} (l/min)	0.075	0.123	0.205	0.153	0.101	0.088
v_{tr} (l/min)	8.82	14.04	22.89	17.57	11.46	9.95
v_{qr} (l/min)	11.59	18.83	31.06	23.67	15.53	13.33
v_{sr} (l/min)	3.90	3.92	3.90	3.92	3.91	3.92
$V_{scrubber}$ (l)	16.90	19.48	23.75	11.50	13.29	11.77
RUNNING TIME (sec)	259.69	298.3	365.14	175.76	254.96	180.43
time at plug	200.26	-	-	162.03	241.23	150.77
filter flow time	259.69	298.3	365.14	175.76	223.65	180.43
RESIDENCE TIME						
l (inches)	10	10	10	10	10	10
V_e (cm3)	8.48	8.48	8.48	8.48	8.48	8.48
V_r (cm3)	977.51	977.51	977.51	977.51	977.51	977.51
u_i (cm/min)	0.87	1.44	2.41	1.80	1.18	1.04
u_t (cm/min)	0.90	1.43	2.33	1.79	1.17	1.02
τ_p (sec)	1.74	1.06	0.63	0.84	1.29	1.46
τ (sec)	1.70	1.07	0.65	0.85	1.30	1.50
τ_{ave} (sec)	**1.72**	**1.06**	**0.64**	**0.85**	**1.29**	**1.48**
NO mean (ppm)	-	-	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-	-	-
NO total (ppm)	24.6628	22.7169	7.8614	4.7280	21.7957	12.1984
g N as NO/ g fuel N (eqn. D.11)	**17.38%**	**15.80%**	**7.07%**	**9.00%**	**16.78%**	**14.72%**
Weight Data						
BL feed weight (g)	1.4864	2.4249	3.0772	1.1147	1.8053	0.9933
fuel N (g)	**0.0016**	**0.0027**	**0.0034**	**0.0012**	**0.0020**	**0.0011**
mass flowrate (g/min)	0.4453	0.4877	0.5056	0.4128	0.4490	0.3953
char weight (g)	0.7824	1.1821	1.2463	0.3296	1.0202	0.3594
char yield	52.64%	48.75%	40.50%	29.57%	56.51%	36.18%
Ammonia absorption						
NH3 in solution (mg)	0.0096	0.0039	0.0010	0.0012	0.0054	0.0014
g N as NH3/ g fuel N	**2.49%**	**1.00%**	**0.32%**	**0.83%**	**1.91%**	**0.63%**
Total Nitrogen Analysis						
% weight char-N	**0.1011%**	**0.1135%**	**0.1146%**	**0.0988%**	**0.1010%**	**0.0966%**
char-N (g)	0.00079	0.00134	0.00143	0.00033	0.00103	0.00035
g char-N/ g fuel N	**47.94%**	**49.85%**	**41.81%**	**26.32%**	**51.42%**	**31.49%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	*44*	*51*	*53*	*54*	*55*	*56*
RESIDENCE TIME	*1.75*	*0.5*	*0.75*	*1*	*2*	*2*
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	25.4	27.5	27	26.4	27	26.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 44**	**PPY 51**	**PPY 53**	**PPY 54**	**PPY 55**	**PPY 56**
v_{pr} (l/min)	0.075	0.187	0.119	0.091	0.087	0.092
v_{tr} (l/min)	8.76	20.88	13.82	10.32	10.36	10.33
v_{qr} (l/min)	11.68	28.08	18.66	13.95	13.92	13.87
v_{sr} (l/min)	3.89	3.90	3.94	3.90	3.93	3.91
$V_{scrubber}$ (l)	11.54	21.32	19.00	19.28	10.11	11.35
RUNNING TIME (sec)	178.07	328.18	288.97	296.77	154.12	174.06
time at plug	103.53	-	280.62	232.67	109.79	164.17
filter flow time	178.07	328.18	288.97	296.77	154.12	174.06
RESIDENCE TIME						
l (inches)	10	7	7	7	14	14
Ve (cm3)	8.48	5.94	5.94	5.94	11.87	11.87
Vr (cm3)	977.51	684.26	684.26	684.26	1368.51	1368.51
u_i (cm/min)	0.88	2.19	1.39	1.07	1.02	1.08
u_t (cm/min)	0.89	2.12	1.40	1.05	1.05	1.05
τ_p (sec)	1.74	0.49	0.77	1.00	2.09	1.97
τ (sec)	1.70	0.50	0.76	1.02	2.03	2.03
τ_{ave} **(sec)**	**1.72**	**0.50**	**0.76**	**1.01**	**2.06**	**2.00**
NO mean (ppm)	-	2.2324	5.7648	9.9042	-	-
g N as NO/ g fuel N (eqn. D.10)	-	17.57%	19.55%	34.10%	-	-
NO total (ppm)	8.2009	10.4049	22.7542	23.6760	5.9283	12.0588
g N as NO/ g fuel N (eqn. D.11)	**13.95%**	**14.97%**	**16.50%**	**21.02%**	**13.35%**	**15.81%**
Weight Data						
BL feed weight (g)	0.6189	1.7393	2.2941	1.4029	0.5522	0.9471
fuel N (g)	**0.0007**	**0.0019**	**0.0025**	**0.0016**	**0.0006**	**0.0011**
mass flowrate (g/min)	0.3587	0.3180	0.4905	0.2836	0.3018	0.3461
char weight (g)	0.2366	1.0562	1.1639	0.8406	0.304	0.5409
char yield	38.23%	60.73%	50.73%	59.92%	55.05%	57.11%
Ammonia absorption						
NH3 in solution (mg)	0.0007	0.0059	0.0069	0.0087	0.0032	0.0033
g N as NH_3/ g fuel N	**0.46%**	**3.17%**	**1.85%**	**2.87%**	**2.69%**	**1.59%**
Total Nitrogen Analysis						
% weight char-N	**0.0890%**	**0.1059%**	**0.0994%**	**0.1062%**	**0.0878%**	**0.1052%**
char-N (g)	0.00021	0.00112	0.00116	0.00089	0.00027	0.00057
g char-N/ g fuel N	**30.65%**	**57.94%**	**45.43%**	**57.33%**	**43.55%**	**54.13%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	*61*	*62*	*63*	*64*	*66*	*75*
RESIDENCE TIME	*1.25*	*1.5*	*1.5*	*2*	*2.2*	*2*
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	28.9	29.7	29.2	29.8	30.1	25.5
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 61**	**PPY 62**	**PPY 63**	**PPY 64**	**PPY 66**	**PPY 75**
v_{pr} (l/min)	0.137	0.119	0.120	0.114	0.108	0.101
v_{tr} (l/min)	16.48	13.70	13.56	13.31	12.30	11.88
v_{qr} (l/min)	22.18	18.49	18.50	17.29	16.18	16.02
v_{sr} (l/min)	3.92	3.97	3.99	4.82	4.40	4.95
$V_{scrubber}$ (l)	19.42	9.21	19.83	11.09	17.85	24.51
RUNNING TIME (sec)	297.59	174.77	298.08	166.32	243.21	299.18
time at plug	-	137.42	-	144.18	233.27	280.89
filter flow time	297.59	174.77	298.08	137.97	243.21	299.18
RESIDENCE TIME						
l (inches)	14	14	14	18	18	16
Ve (cm3)	11.87	11.87	11.87	15.26	15.26	13.57
Vr (cm3)	1368.51	1368.51	1368.51	1759.52	1759.52	1564.01
u_i (cm/min)	1.60	1.39	1.39	1.32	1.26	1.19
u_t (cm/min)	1.66	1.38	1.37	1.34	1.24	1.21
τ_p (sec)	1.33	1.54	1.53	2.08	2.18	2.04
τ (sec)	1.28	1.55	1.56	2.05	2.22	2.01
τ_{ave} **(sec)**	**1.31**	**1.54**	**1.55**	**2.06**	**2.20**	**2.03**
NO mean (ppm)	-	-	5.6333	4.0884	-	3.8667
g N as NO/ g fuel N (eqn. D.10)	-	-	20.16%	15.84%	-	14.11%
NO total (ppm)	20.6476	8.1997	23.1198	6.7207	9.2386	15.4604
g N as NO/ g fuel N (eqn. D.11)	**17.91%**	**15.77%**	**16.65%**	**10.83%**	**8.14%**	**12.05%**
Weight Data						
BL feed weight (g)	2.2673	0.8498	2.2628	0.9631	1.6390	1.8419
fuel N (g)	**0.0025**	**0.0009**	**0.0025**	**0.0011**	**0.0018**	**0.0020**
mass flowrate (g/min)	0.4571	0.3710	0.4555	0.4008	0.4216	0.3934
char weight (g)	1.2568	0.4644	1.2437	0.5277	0.8264	0.9759
char yield	55.43%	54.65%	54.96%	54.79%	50.42%	52.98%
Ammonia absorption						
NH3 in solution (mg)	0.0042	0.0041	0.0073	0.0028	0.0223	0.0043
g N as NH3/ g fuel N	**1.37%**	**3.65%**	**1.91%**	**1.66%**	**6.52%**	**0.98%**
Total Nitrogen Analysis						
% weight char-N	**0.0921%**	**0.0747%**	**0.0900%**	**0.1049%**	**0.1046%**	**0.0996%**
char-N (g)	0.00116	0.00035	0.00112	0.00055	0.00086	0.00097
g char-N/ g fuel N	**45.99%**	**36.78%**	**44.56%**	**51.78%**	**47.51%**	**47.54%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	*81*	*82*	*93*	*94*	*95*	*96*
RESIDENCE TIME	*1.25*	*1.75*	*0.5*	*0.75*	*0.75*	*0.5*
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	25	25	28.9	28.1	28.3	27.2
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 81**	**PPY 82**	**PPY 93**	**PPY 94**	**PPY 95**	**PPY 96**
v_{pr} (l/min)	0.122	0.089	0.178	0.121	0.121	0.180
v_{tr} (l/min)	14.27	10.23	20.94	14.03	14.03	20.97
v_{qr} (l/min)	18.30	13.77	28.16	18.77	18.74	28.09
v_{sr} (l/min)	4.91	4.95	4.96	4.89	4.88	4.97
$V_{scrubber}$ (l)	27.23	16.41	24.43	14.55	22.56	29.62
RUNNING TIME (sec)	333.01	199	295.34	178.35	277.38	357.95
time at plug	-	186.81	-	154.07	271.28	-
filter flow time	333.01	199	295.34	178.35	277.38	357.95
RESIDENCE TIME						
l (inches)	12	12	7	7	7	7
Ve (cm3)	10.18	10.18	5.94	5.94	5.94	5.94
Vr (cm3)	1173.01	1173.01	684.26	684.26	684.26	684.26
u_i (cm/min)	1.44	1.05	2.08	1.41	1.41	2.11
u_t (cm/min)	1.46	1.05	2.11	1.42	1.42	2.13
τ_p (sec)	1.27	1.74	0.51	0.76	0.75	0.51
τ_t (sec)	1.25	1.75	0.50	0.75	0.75	0.50
τ_{ave} (sec)	**1.26**	**1.75**	**0.51**	**0.75**	**0.75**	**0.50**
NO mean (ppm)	5.6906	-	-	-	4.2988	1.8617
g N as NO/ g fuel N (eqn. D.10)	22.26%	-	-	-	20.10%	14.63%
NO total (ppm)	26.8416	17.8209	-	-	15.2570	8.4594
g N as NO/ g fuel N (eqn. D.11)	**18.91%**	**17.75%**	-	-	**15.78%**	**11.14%**
Weight Data						
BL feed weight (g)	2.3835	1.2423	1.8273	0.8494	1.6160	1.9065
fuel N (g)	**0.0026**	**0.0014**	**0.0020**	**0.0009**	**0.0018**	**0.0021**
mass flowrate (g/min)	0.4294	0.3990	0.3712	0.3308	0.3574	0.3196
char weight (g)	1.2822	0.7039	1.0083	0.4258	0.8556	1.2238
char yield	53.79%	56.66%	55.18%	50.13%	52.95%	64.19%
Ammonia absorption						
NH3 in solution (mg)	0.0108	0.0182	0.0119	0.0042	0.0072	0.0037
g N as NH_3/ g fuel N	**2.24%**	**5.27%**	**4.80%**	**2.43%**	**2.21%**	**1.42%**
Total Nitrogen Analysis						
% weight char-N	**0.0800%**	**0.0930%**	**0.1025%**	**0.0943%**	**0.0891%**	**0.0970%**
char-N (g)	0.00103	0.00065	0.00103	0.00040	0.00076	0.00119
g char-N/ g fuel N	**38.77%**	**47.47%**	**50.95%**	**42.59%**	**42.50%**	**56.09%**

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	***98***	***104***	***106***	***107***	***108***	***109***
RESIDENCE TIME	***1***	***1.75***	***1.75***	***2.25***	***2.5***	***1.75***
TEMPERATURE (C)	900	900	900	900	900	900
ROOM TEMPERATURE (C)	31.5	28	30.3	31.4	29.6	28.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 98**	**PPY 104**	**PPY 106**	**PPY 107**	**PPY 108**	**PPY 109**
v_{pr} (l/min)	0.093	0.146	0.148	0.114	0.105	0.147
v_{tr} (l/min)	10.37	16.99	17.01	13.21	11.95	17.05
v_{qr} (l/min)	13.98	23.00	22.84	17.76	16.10	22.73
v_{sr} (l/min)	4.96	4.98	4.98	4.97	4.98	4.98
$V_{scrubber}$ (l)	17.72	25.63	22.85	14.61	24.86	15.46
RUNNING TIME (sec)	214.37	308.96	275.29	176.37	297.09	186.25
time at plug	200.64	-	269.19	170.33	-	181.75
filter flow time	214.37	308.96	275.29	176.37	297.09	186.25
RESIDENCE TIME						
l (inches)	7	20	20	20	20	20
Ve (cm3)	5.94	16.96	16.96	16.96	16.96	16.96
Vr (cm3)	684.26	1955.02	1955.02	1955.02	1955.02	1955.02
u_i (cm/min)	1.07	1.71	1.71	1.32	1.22	1.72
u_t (cm/min)	1.04	1.72	1.71	1.32	1.20	1.72
τ_p (sec)	1.00	1.79	1.78	2.31	2.50	1.78
τ (sec)	1.03	1.77	1.78	2.31	2.53	1.77
τ_{ave} **(sec)**	**1.01**	**1.78**	**1.78**	**2.31**	**2.52**	**1.77**
NO mean (ppm)	-	3.2621	1.4888	-	3.8753	3.0290
g N as NO/ g fuel N (eqn. D.10)	-	16.75%	8.49%	-	12.14%	16.47%
NO total (ppm)	12.9339	14.3986	5.5010	6.1488	16.2167	7.4772
g N as NO/ g fuel N (eqn. D.11)	**17.78%**	**14.36%**	**6.99%**	**9.31%**	**10.26%**	**13.42%**
Weight Data						
BL feed weight (g)	0.8939	2.0469	1.5883	1.0322	2.2510	1.1298
fuel N (g)	**0.0010**	**0.0023**	**0.0018**	**0.0011**	**0.0025**	**0.0013**
mass flowrate (g/min)	0.2673	0.3975	0.3540	0.3636	0.4546	0.3730
char weight (g)	0.4699	1.0172	0.7792	0.4722	1.1934	0.5318
char yield	52.57%	49.69%	49.06%	45.75%	53.02%	47.07%
Ammonia absorption						
NH3 in solution (mg)	0.0026	-	-	-	-	-
g N as NH_3/ g fuel N	**1.05%**	-	-	-	-	-
Total Nitrogen Analysis						
% weight char-N	**0.0869%**					
char-N (g)	0.00041					
g char-N/ g fuel N	**41.15%**					

Table D.3. Nitrogen Evolution at 900 C in the LEFR (continued)

EXPERIMENT #	***125***	***126***	***127***	***128***
RESIDENCE TIME	***3***	***3.75***	***3.75***	***3.75***
TEMPERATURE (C)	900	900	900	900
ROOM TEMPERATURE (C)	27.4	28.4	31.3	31.3
FEED GAS	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 125**	**PPY 126**	**PPY 127**	**PPY 128**
v_{pr} (l/min)	0.130	0.105	0.106	0.106
v_{tr} (l/min)	14.98	12.09	12.04	12.01
v_{qr} (l/min)	20.15	15.88	16.02	16.00
v_{sr} (l/min)	-	-	-	-
$V_{scrubber}$ (l)	-	-	-	-
RUNNING TIME (sec)	204.82	195.37	129.24	146.04
time at plug	198.72	185.48	120.89	137.7
filter flow time	-	-	-	-
RESIDENCE TIME				
l (inches)	30	30	30	30
Ve (cm3)	25.44	25.44	25.44	25.44
Vr (cm3)	2932.53	2932.53	2932.53	2932.53
u_i (cm/min)	1.52	1.23	1.22	1.22
u_t (cm/min)	1.52	1.22	1.21	1.20
τ_p (sec)	3.00	3.73	3.75	3.74
τ_t (sec)	3.01	3.74	3.79	3.80
τ_{ave} (sec)	**3.01**	**3.73**	**3.77**	**3.77**
NO mean (ppm)	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-
NO total (ppm)	3.9906	2.9728	1.6857	1.8741
g N as NO/ g fuel N (eqn. D.11)	**5.72%**	**3.61%**	**3.43%**	**3.24%**
Weight Data				
BL feed weight (g)	1.2536	1.1756	0.6960	0.8179
fuel N (g)	**0.0014**	**0.0013**	**0.0008**	**0.0009**
mass flowrate (g/min)	0.3785	0.3803	0.3454	0.3564
char weight (g)	0.6413	0.5281	0.3194	0.4031
char yield	51.16%	44.92%	45.89%	49.28%
Ammonia absorption				
NH3 in solution (mg)	-	-	-	-
g N as NH3/ g fuel N	-	-	-	-
Total Nitrogen Analysis				
% weight char-N				
char-N (g)				
g char-N/ g fuel N				

Table D.4. Nitrogen Evolution at 800 C in the LEFR

EXPERIMENT #	*59*	*60*	*77*	*83*	*84*	*85*
RESIDENCE TIME	*2*	*2*	*2*	*1.5*	*1.75*	*1.25*
TEMPERATURE (C)	800	800	800	800	800	800
ROOM TEMPERATURE (C)	31.1	29.9	23.5	29.4	29.8	28.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 59**	**PPY 60**	**PPY 77**	**PPY 83**	**PPY 84**	**PPY 85**
v_{pr} (l/min)	0.098	0.099	0.112	0.113	0.098	0.133
v_{tr} (l/min)	11.31	11.53	13.01	12.82	11.30	15.60
v_{qr} (l/min)	15.12	15.27	17.25	17.20	14.91	20.78
v_{sr} (l/min)	3.92	3.97	4.93	4.95	4.97	4.96
$V_{scrubber}$ (l)	19.46	9.77	25.14	19.28	25.00	11.42
RUNNING TIME (sec)	297.64	147.75	306.1	233.77	301.82	143.63
time at plug	-	109.69	-	-	-	138.31
filter flow time	297.64	147.75	306.1	233.77	301.82	143.63
RESIDENCE TIME						
l (inches)	14	14	16	12	12	12
V_c (cm3)	11.87	11.87	13.57	10.18	10.18	10.18
V_r (cm3)	1368.51	1368.51	1564.01	1173.01	1173.01	1173.01
u_i (cm/min)	1.04	1.05	1.21	1.21	1.04	1.42
u_t (cm/min)	1.04	1.06	1.22	1.18	1.04	1.44
τ_p (sec)	2.06	2.04	2.02	1.52	1.75	1.29
τ (sec)	2.06	2.01	1.99	1.55	1.76	1.27
τ_{ave} **(sec)**	**2.06**	**2.02**	**2.01**	**1.53**	**1.76**	**1.28**
NO mean (ppm)	-	-	5.5962	-	7.1090	-
g N as NO/ g fuel N (eqn. D.10)	-	-	20.15%	-	20.77%	-
NO total (ppm)	31.3061	7.7950	25.4098	15.8043	28.6701	3.5011
g N as NO/ g fuel N (eqn. D.11)	**19.59%**	**15.28%**	**17.93%**	**15.62%**	**16.65%**	**10.20%**
Weight Data						
BL feed weight (g)	2.1337	0.6935	2.2216	1.5430	2.2900	0.6364
fuel N (g)	**0.0024**	**0.0008**	**0.0025**	**0.0017**	**0.0025**	**0.0007**
mass flowrate (g/min)	0.4301	0.3793	0.4355	0.3960	0.4552	0.2761
char weight (g)	1.2951	0.379	1.2175	0.8928	1.3243	0.3168
char yield	60.70%	54.65%	54.80%	57.86%	57.83%	49.78%
Ammonia absorption						
NH3 in solution (mg)	0.0091	0.0041	0.0037	0.0190	0.0190	0.0076
g N as NH3/ g fuel N	**2.12%**	**2.95%**	**0.76%**	**5.56%**	**3.25%**	**6.72%**
Total Nitrogen Analysis						
% weight char-N	**0.0971%**	**0.1002%**	**0.0892%**	**0.0946%**	**0.0986%**	**0.0972%**
char-N (g)	0.00126	0.00038	0.00109	0.00084	0.00131	0.00031
g char-N/ g fuel N	**53.10%**	**49.33%**	**44.04%**	**49.31%**	**51.37%**	**43.59%**

Table D.4. Nitrogen Evolution at 800 C in the LEFR (continued)

EXPERIMENT #	***86***	***87***	***101***	***102***	***103***	***110***
RESIDENCE TIME	***1.25***	***1.25***	***1***	***0.75***	***0.5***	***2.75***
TEMPERATURE (C)	800	800	800	800	800	800
ROOM TEMPERATURE (C)	28.6	28.6	31.5	31.8	30.5	27
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 86**	**PPY 87**	**PPY 101**	**PPY 102**	**PPY 103**	**PPY 110**
v_{pr} (l/min)	0.133	0.133	0.101	0.130	0.180	0.105
v_{tr} (l/min)	15.53	15.31	11.33	15.02	20.98	11.84
v_{qr} (l/min)	20.75	20.73	15.15	21.29	28.07	15.86
v_{sr} (l/min)	4.93	4.58	4.97	4.97	4.98	-
$V_{scrubber}$ (l)	11.36	22.08	24.45	21.67	23.97	-
RUNNING TIME (sec)	138.3	287.76	294.9	261.31	288.63	282.2
time at plug	106.44	264.14	276.66	252.96	280.28	274.57
filter flow time	138.3	272	294.9	261.31	288.63	-
RESIDENCE TIME						
l (inches)	12	12	7	7	7	20
V_e (cm3)	10.18	10.18	5.94	5.94	5.94	16.96
V_r (cm3)	1173.01	1173.01	684.26	684.26	684.26	1955.02
u_i (cm/min)	1.42	1.42	1.07	1.37	1.91	1.12
u_t (cm/min)	1.43	1.41	1.04	1.37	1.93	1.10
τ_p (sec)	1.29	1.29	1.00	0.78	0.56	2.71
τ (sec)	1.27	1.29	1.03	0.78	0.55	2.77
τ_{ave} (sec)	**1.28**	**1.29**	**1.01**	**0.78**	**0.56**	**2.74**
NO mean (ppm)	-	2.9323	-	2.0017	0.7723	-
g N as NO/ g fuel N (eqn. D.10)	-	14.51%	-	8.68%	4.80%	-
NO total (ppm)	2.4409	9.8974	17.6876	7.4952	3.2949	23.1086
g N as NO/ g fuel N (eqn. D.11)	**8.50%**	**11.12%**	-	**7.71%**	**4.38%**	**18.27%**
Weight Data						
BL feed weight (g)	0.5305	1.6338	1.9773	1.7784	1.8667	1.7946
fuel N (g)	**0.0006**	**0.0018**	**0.0022**	**0.0020**	**0.0021**	**0.0020**
mass flowrate (g/min)	0.2990	0.3711	0.4288	0.4218	0.3996	0.3922
char weight (g)	0.2491	0.8358	1.3161	1.1241	1.1339	1.0387
char yield	46.96%	51.16%	66.56%	63.21%	60.74%	57.88%
Ammonia absorption						
NH3 in solution (mg)	0.0053	0.0080	0.0036	0.0026	0.0031	-
g N as NH3/ g fuel N	**5.45%**	**2.84%**	**0.72%**	**0.78%**	**1.20%**	-
Total Nitrogen Analysis						
% weight char-N	**0.0831%**	**0.0949%**				
char-N (g)	0.00021	0.00079				
g char-N/ g fuel N	**35.15%**	**43.74%**				

Table D.4. Nitrogen Evolution at 800 C in the LEFR (continued)

EXPERIMENT #	*111*	*112*	*113*	*115*	*116*	*122*
RESIDENCE TIME	***2.25***	***2.25***	***2.25***	***2.5***	***2.5***	***3.25***
TEMPERATURE (C)	800	800	800	800	800	800
ROOM TEMPERATURE (C)	27.6	29.4	30.5	30.4	29.9	27.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 111**	**PPY 112**	**PPY 113**	**PPY 115**	**PPY 116**	**PPY 122**
v_{pr} (l/min)	0.124	0.125	0.125	0.114	0.116	0.133
v_{tr} (l/min)	14.45	14.33	14.47	13.04	13.11	15.12
v_{qr} (l/min)	19.11	19.16	19.07	17.05	17.56	20.37
v_{sr} (l/min)	-	-	-	-	-	-
$V_{scrubber}$ (l)	-	-	-	-	-	-
RUNNING TIME (sec)	264.58	232.56	299.78	327.96	298.9	150.66
time at plug	258.48	228	-	-	-	144.62
filter flow time	-	-	-	-	-	-
RESIDENCE TIME						
l (inches)	20	20	20	20	20	30
V_c (cm3)	16.96	16.96	16.96	16.96	16.96	25.44
V_r (cm3)	1955.02	1955.02	1955.02	1955.02	1955.02	2932.53
u_i (cm/min)	1.33	1.32	1.33	1.21	1.23	1.42
u_t (cm/min)	1.34	1.32	1.33	1.20	1.21	1.40
τ_p (sec)	2.30	2.30	2.29	2.52	2.49	3.22
τ_t (sec)	2.27	2.31	2.29	2.55	2.53	3.26
τ_{ave} **(sec)**	**2.29**	**2.30**	**2.29**	**2.53**	**2.51**	**3.24**
NO mean (ppm)	-	-	4.3951	-	5.7909	-
g N as NO/ g fuel N (eqn. D.10)	-	-	19.26%	-	20.54%	-
NO total (ppm)	14.2731	12.6182	17.9900	25.2559	23.9885	5.0121
g N as NO/ g fuel N (eqn. D.11)	**16.18%**	**15.77%**	**15.78%**	**17.87%**	**17.08%**	**12.34%**
Weight Data						
BL feed weight (g)	1.5136	1.3611	1.9359	2.1538	2.1851	0.7370
fuel N (g)	**0.0017**	**0.0015**	**0.0021**	**0.0024**	**0.0024**	**0.0008**
mass flowrate (g/min)	0.3513	0.3582	0.3875	0.3940	0.4386	0.3058
char weight (g)	0.7922	0.7143	0.9937	1.2174	1.1791	0.3672
char yield	52.34%	52.48%	51.33%	56.52%	53.96%	49.82%
Ammonia absorption						
NH3 in solution (mg)	-	-	-	-	-	-
g N as NH_3/ g fuel N	-	-	-	-	-	-
Total Nitrogen Analysis						
% weight char-N						
char-N (g)						
g char-N/ g fuel N						

Table D.4. Nitrogen Evolution at 800 C in the LEFR (continued)

EXPERIMENT #	*123*	*124*	*134*	*135*	*136*	*137*
RESIDENCE TIME	***3.25***	***4***	***4***	***3.5***	***3.25***	***3.25***
TEMPERATURE (C)	800	800	800	800	800	800
ROOM TEMPERATURE (C)	28.4	31.3	33.6	31.5	31.2	31.6
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 123**	**PPY 124**	**PPY 134**	**PPY 135**	**PPY 136**	**PPY 137**
v_{pr} (l/min)	0.132	0.107	0.109	0.122	0.132	0.136
v_{tr} (l/min)	15.13	12.27	12.30	13.93	15.12	15.15
v_{qr} (l/min)	20.20	16.20	16.25	19.35	20.09	19.96
v_{sr} (l/min)	-	-	-	-	-	-
$V_{scrubber}$ (l)	-	-	-	-	-	-
RUNNING TIME (sec)	315.05	166.31	232.12	190.43	160.88	163.51
time at plug	-	166.31	225.97	186.64	144.84	155.05
filter flow time	-	-	-	-	-	-
RESIDENCE TIME						
l (inches)	30	30	30	30	30	30
Ve (cm3)	25.44	25.44	25.44	25.44	25.44	25.44
Vr (cm3)	2932.53	2932.53	2932.53	2932.53	2932.53	2932.53
u_i (cm/min)	1.41	1.13	1.14	1.29	1.40	1.44
u_t (cm/min)	1.40	1.12	1.12	1.27	1.39	1.39
τ_p (sec)	3.25	4.04	4.00	3.55	3.27	3.18
τ_t (sec)	3.27	4.07	4.09	3.59	3.30	3.30
τ_{ave} (sec)	**3.26**	**4.05**	**4.04**	**3.57**	**3.28**	**3.24**
NO mean (ppm)	-	-	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-	-	-	-
NO total (ppm)	17.3515	6.5917	11.2748	9.2782	4.5814	6.6119
g N as NO/ g fuel N (eqn. D.11)	**14.95%**	**10.26%**	**11.81%**	**14.30%**	**12.42%**	**14.08%**
Weight Data						
BL feed weight (g)	2.0899	0.9238	1.3654	1.0897	0.6561	0.8317
fuel N (g)	**0.0023**	**0.0010**	**0.0015**	**0.0012**	**0.0007**	**0.0009**
mass flowrate (g/min)	0.3980	0.3333	0.3625	0.3503	0.2718	0.3218
char weight (g)	1.1189	0.4541	0.7336	0.6011	0.3193	0.4327
char yield	53.54%	49.16%	53.73%	55.16%	48.67%	52.03%
Ammonia absorption						
NH3 in solution (mg)	-	-	-	-	-	-
g N as NH3/ g fuel N	-	-	-	-	-	-
Total Nitrogen Analysis						
% weight char-N						
char-N (g)						
g char-N/ g fuel N						

Table D.5. Nitrogen Evolution at 700 C in the LEFR

EXPERIMENT #	***57***	***58***	***79***	***88***	***89***	***99***
RESIDENCE TIME	***2***	***2***	***2***	***1.5***	***1.75***	***1***
TEMPERATURE (C)	700	700	700	700	700	700
ROOM TEMPERATURE (C)	29.2	30.8	23.3	28.6	27.3	29.5
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 57**	**PPY 58**	**PPY 79**	**PPY 88**	**PPY 89**	**PPY 99**
v_{pr} (l/min)	0.106	0.108	0.124	0.119	0.103	0.106
v_{tr} (l/min)	12.57	12.54	14.30	14.06	11.95	12.09
v_{qr} (l/min)	16.83	16.71	19.03	17.69	16.06	16.44
v_{sr} (l/min)	3.62	3.87	4.96	4.96	-	4.97
$V_{scrubber}$ (l)	18.26	12.72	24.81	25.50	-	18.00
RUNNING TIME (sec)	300.22	196.96	297.81	308.46	315	217.23
time at plug	-	180.98	-	-	152.58	214.92
filter flow time	300.22	196.96	297.81	308.46	-	217.23
RESIDENCE TIME						
l (inches)	14	14	16	12	12	7
Ve (cm3)	11.87	11.87	13.57	10.18	10.18	5.94
Vr (cm3)	1368.51	1368.51	1564.01	1173.01	1173.01	684.26
u_i (cm/min)	1.02	1.03	1.22	1.15	1.00	1.02
u_t (cm/min)	1.05	1.04	1.22	1.18	1.01	1.01
τ_p (sec)	2.10	2.06	2.00	1.59	1.83	1.04
τ (sec)	2.03	2.05	2.00	1.55	1.82	1.06
τ_{ave} (sec)	**2.06**	**2.05**	**2.00**	**1.57**	**1.82**	**1.05**
NO mean (ppm)	4.1025	-	2.7555	1.8620	-	0.9469
g N as NO/ g fuel N (eqn. D.10)	15.19%	-	11.36%	7.11%	-	3.85%
NO total (ppm)	16.2770	8.4163	12.1064	9.9693	5.3847	2.7103
g N as NO/ g fuel N (eqn. D.11)	**12.04%**	**10.55%**	**10.05%**	**7.40%**	**7.03%**	**3.08%**
Weight Data						
BL feed weight (g)	2.0207	1.1807	2.0817	2.1772	1.0973	1.2763
fuel N (g)	**0.0022**	**0.0013**	**0.0023**	**0.0024**	**0.0012**	**0.0014**
mass flowrate (g/min)	0.4038	0.3914	0.4194	0.4235	0.4315	0.3563
char weight (g)	1.4635	0.7334	1.1872	1.3427	0.6716	0.8436
char yield	72.43%	62.12%	57.03%	61.67%	61.20%	66.10%
Ammonia absorption						
NH3 in solution (mg)	0.0039844	0.0037276	0.003695	0.004957	-	0.009587
g N as NH3/ g fuel N	**1.18%**	**1.77%**	**0.88%**	**1.08%**	-	**3.20%**
Total Nitrogen Analysis						
% weight char-N	0.0891%	0.0969%	0.0917%	0.0940%	0.0940%	
char-N (g)	0.00130	0.00071	0.00109	0.00126	0.00063	
g char-N/ g fuel N	**58.14%**	**54.23%**	**47.11%**	**52.23%**	**51.83%**	

Table D.5. Nitrogen Evolution at 700 C in the LEFR (continued)

EXPERIMENT #	*100*	*117*	*118*	*119*	*120*	*129*
RESIDENCE TIME	*0.75*	*2.5*	*1.75*	*2.75*	*2.25*	*3.5*
TEMPERATURE (C)	700	700	700	700	700	700
ROOM TEMPERATURE (C)	30.5	27.4	26.8	26.4	25.3	28.4
FEED GAS	N2	N2	N2	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125	90-125	90-125	90-125
Data Acquisition File	**PPY 100**	**PPY 117**	**PPY 118**	**PPY 119**	**PPY 120**	**PPY 129**
v_{pr} (l/min)	0.139	0.122	0.172	0.114	0.133	0.134
v_{tr} (l/min)	16.05	14.18	19.84	12.90	15.48	15.18
v_{qr} (l/min)	21.12	18.97	26.79	17.08	20.62	19.96
v_{sr} (l/min)	4.97	-	-	-	-	-
$V_{scrubber}$ (l)	15.86	-	-	-	-	-
RUNNING TIME (sec)	191.36	311.26	310.05	186.42	299.62	165.99
time at plug	186.8	305.16	-	182.57	-	162.2
filter flow time	191.36	-	-	-	-	-
RESIDENCE TIME						
l (inches)	7	20	20	20	20	30
Ve (cm3)	5.94	16.96	16.96	16.96	16.96	25.44
Vr (cm3)	684.26	1955.02	1955.02	1955.02	1955.02	2932.53
u_i (cm/min)	1.33	1.19	1.67	1.11	1.30	1.29
u_t (cm/min)	1.34	1.19	1.67	1.09	1.31	1.27
τ_p (sec)	0.80	2.57	1.83	2.75	2.35	3.53
τ_t (sec)	0.80	2.55	1.82	2.80	2.32	3.59
τ_{ave} (sec)	**0.80**	**2.56**	**1.82**	**2.77**	**2.34**	**3.56**
NO mean (ppm)	0.2659	-	-	-	-	-
g N as NO/ g fuel N (eqn. D.10)	1.21%	-	-	-	-	-
NO total (ppm)	0.7320	14.0400	5.4901	9.1175	10.9349	6.8893
g N as NO/ g fuel N (eqn. D.11)	**1.07%**	**11.75%**	**7.08%**	**13.20%**	**10.13%**	**13.45%**
Weight Data						
BL feed weight (g)	1.2852	2.0271	1.8543	1.0624	2.0071	0.9178
fuel N (g)	**0.0014**	**0.0023**	**0.0021**	**0.0012**	**0.0022**	**0.0010**
mass flowrate (g/min)	0.4128	0.3986	0.3588	0.3491	0.4019	0.3395
char weight (g)	0.7992	1.1772	1.0422	0.6266	1.0803	0.4772
char yield	62.18%	58.07%	56.20%	58.98%	53.82%	51.99%
Ammonia absorption						
NH3 in solution (mg)	0.001663	-	-	-	-	-
g N as NH3/ g fuel N	**0.72%**	-	-	-	-	-
Total Nitrogen Analysis						
% weight char-N						
char-N (g)						
g char-N/ g fuel N						

Table D.5. Nitrogen Evolution at 700 C in the LEFR (continued)

EXPERIMENT #	***130***	***132***	***133***
RESIDENCE TIME	***4***	***3.5***	***3.25***
TEMPERATURE (C)	700	700	700
ROOM TEMPERATURE (C)	36	34.2	33.9
FEED GAS	N2	N2	N2
PARTICLE SIZE (um)	90-125	90-125	90-125
Data Acquisition File	**PPY 130**	**PPY 132**	**PPY 133**
v_{pr} (l/min)	0.117	0.132	0.145
v_{tr} (l/min)	13.28	15.15	16.40
v_{qr} (l/min)	17.68	20.08	21.58
v_{sr} (l/min)	-	-	-
$V_{scrubber}$ (l)	-	-	-
RUNNING TIME (sec)	239.48	303.51	180.54
time at plug	235.63	-	175.16
filter flow time	-	-	-
RESIDENCE TIME			
l (inches)	30	30	30
Ve (cm3)	25.44	25.44	25.44
Vr (cm3)	2932.53	2932.53	2932.53
u_i (cm/min)	1.10	1.25	1.38
u_t (cm/min)	1.09	1.25	1.35
τ_p (sec)	4.14	3.65	3.32
τ (sec)	4.21	3.67	3.39
τ_{ave} (sec)	**4.18**	**3.66**	**3.35**
NO mean (ppm)	-	-	-
g N as NO/ g fuel N (eqn. D.10)	-	-	-
NO total (ppm)	16.8983	15.9830	5.9810
g N as NO/ g fuel N (eqn. D.11)	**16.01%**	**14.19%**	**13.87%**
Weight Data			
BL feed weight (g)	1.6247	1.9841	0.8202
fuel N (g)	**0.0018**	**0.0022**	**0.0009**
mass flowrate (g/min)	0.4137	0.3922	0.2810
char weight (g)	0.9479	1.0787	0.4483
char yield	58.34%	54.37%	54.66%
Ammonia absorption			
NH3 in solution (mg)	-	-	-
g N as NH3/ g fuel N	-	-	-
Total Nitrogen Analysis			
% weight char-N			
char-N (g)			
g char-N/ g fuel N			

Appendix E
Preliminary Results

E.1 Experiments using the old injector

Experiments # 1 through 18 in **Table** A.1 in **Appendix A** were preliminary experiments made using the old injector. In this part of the study, NO and NH_3 levels in black liquor pyrolysis were measured. The procedure used in removing the remaining black liquor particles from the feed system after each experiment differed from that which was presented in **Chapter 4**. For these experiments, the feed system was flushed with a high primary flow rate without collecting the char and fume particles. Furthermore, the injector was not cleaned after each run. The experimental procedure used in this set of runs will be referred to as the "old" experimental procedure throughout the text.

These initial experiments were done using the old injector having an inside diameter of 3.34 mm. With this diameter, it was very difficult to maintain equal total gas and primary gas velocities ($u_t = u_i$). The concept of having equal gas velocities will be referred to as 1:1 velocity through out the text. The 1:1 velocity is required to estimate the residence time more accurately. In the experiments, the residence time was not kept constant. **Table** E.1 shows the residence time at each furnace temperature for constant gas flows used -- v_{pr} = 0.1 liters/min, v_{tr} = 13 liters/min, and v_{qr} = 20 liters/min. To maintain 1:1 velocity, one of the following primary and total gas flow rates combination should have been used -- v_{pr} = 0.1 liters/min and v_{tr} = 44 liters/min or v_{pr} = 0.03 liters/min and v_{tr} = 13 liters/min. However, at high total gas flow rates (with v_{tr} = 44 liters/min) , the NO concentration was too diluted and the NO-NO_x meter readings became too small. Also, at $v_{pr} < 0.1$ liters/min, the black liquor particles did not feed very well and thus created several plugging problems. The reported residence times were averages from the one calculated from the primary flow (τ_p) and the one calculated from the total gas flow (τ). The equations are in **Appendix D**. The difference between τ_p and τ is shown in **Table** E.1. Because the difference between the two calculated residence times were

significant, the averaged residence time (τ_{ave}) was a very crude estimation of the actual residence time.

Table E.1. Residence Times for Initial Experiments

Furnace Temperature (°C)	τ_p (seconds)	τ_t (seconds)	τ_{ave} (seconds)	$\tau_t - \tau_p$ (seconds)
700	0.7	2.35	1.52	1.65
800	0.61	2.12	1.37	1.51
900	0.53	1.93	1.23	1.4
1000	0.5	1.78	1.14	1.28
1100	0.487	1.66	1.07	1.17

Table D.1 in **Appendix D** provides a summary of experimental and analytical results based on equations presented in **Appendices C** and **D**. **Figure** E.1 plots the conversion of fuel N to NO against the furnace temperature. The furnace temperatures were 700 - 1100 °C. It was evident from **Figure** E.1 that a maximum for NO formation occurred at 900 °C. The value at 1100 °C shown in the figure was greater than it should have been. It was believed that there was an error made in the black liquor feed weight; it should have been higher than the recorded weight.

For all temperatures except at 900 °C, the total NO formed, designated as NO_{total}, was calculated based on **eqn**.C.2.4 in **Appendix C**. At 900 °C, the average, designated as NO_{mean}, was calculated based on **eqn**.C.2.3. However, it was found that NO_{mean} tends to overestimate NO. Refer to the summarized results in **Appendix D**. The difference between the fraction of fuel N that became NO using NO_{total} and NO_{mean} (**eqn.** D.10 and D.11) were significant in most experiments. Usually, the NO_{mean} was very hard to

calculate because no noticeable steady state was evident in the plots generated from the NO-NO_x meter readings. Thus, NO_{total} was found to be appropriate in analyzing for NO.

Figure E.2 plots the conversion of fuel N to NH_3 against the furnace temperature. The ISE results are included in **Table** A.6*b* in **Appendix A**. The analytical results based on **eqn.** C.1.1 from **Appendix C** and **eqn.** D.12 from **Appendix D** are summarized in **Table** D.1 in **Appendix D**. As mentioned before, the reported value at 1100 °C should have been lower due to the error made in the black liquor feed weight. Although NH_3 was difficult to measure, the data suggest that the method used for analysis was acceptable. NH_3 followed the same trend as NO. The NH_3 formation also peaked at 900 °C. The results were reproducible.

The char yield is plotted in **Figure** E.3. The char yield was defined as the fraction of black liquor feed that became char. The plot clearly shows that the char yield decreased with temperature. In **Figure** E.4, the conversion of fuel nitrogen to char-N is plotted against temperature. The data points in **Figure** E.4 were calculated based on the total nitrogen analysis included in **Table** A.7 in **Appendix A**. The amount of nitrogen retained in the char also decreased with temperature. For **Figures** E.3 and E.4, the char yield and the char-N values at 1100 °C were not included. The relative weight of char-N to char is plotted against temperature in **Figure** E.5. It seemed that the weight of char-N relative to the weight of the char can be assumed constant with temperature.

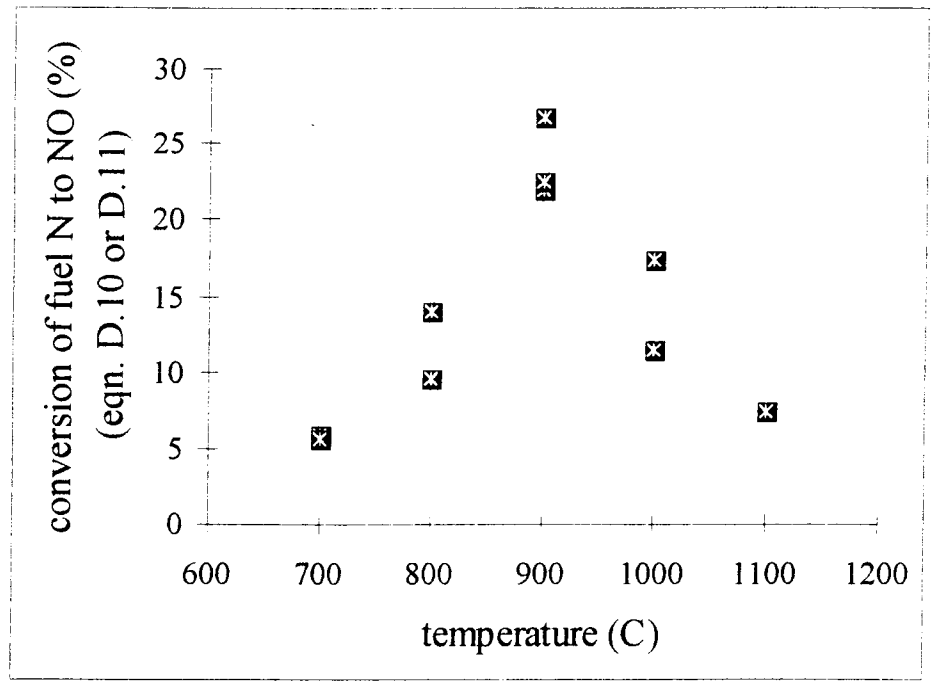


Figure E.1. NO Formation -- Feasibility Studies Using the Old Injector
(residence time = varied)

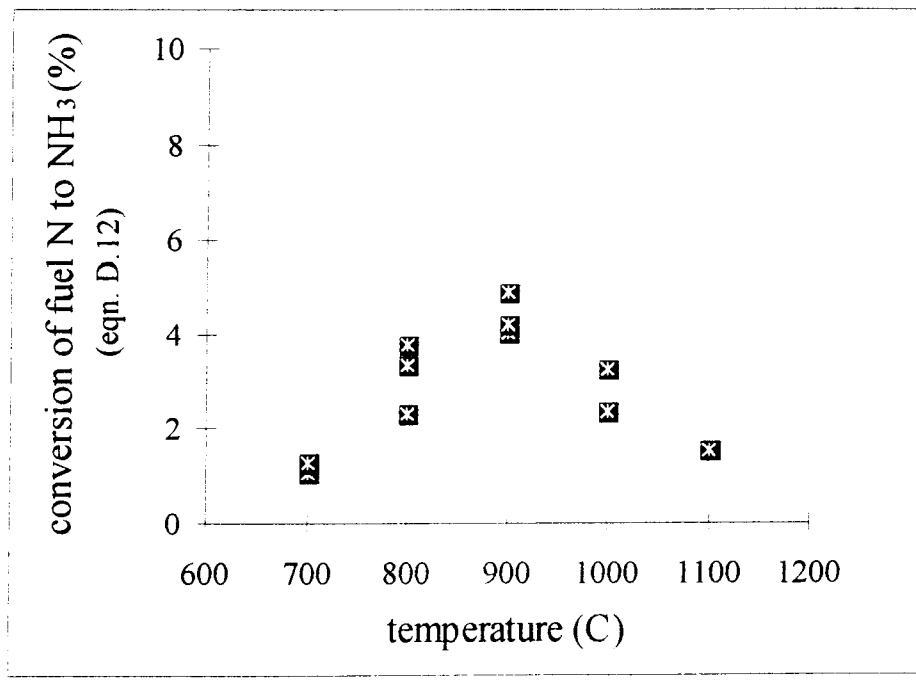


Figure E.2. NH_3 Formation -- Feasibility Studies Using the Old Injector
(residence time = varied)

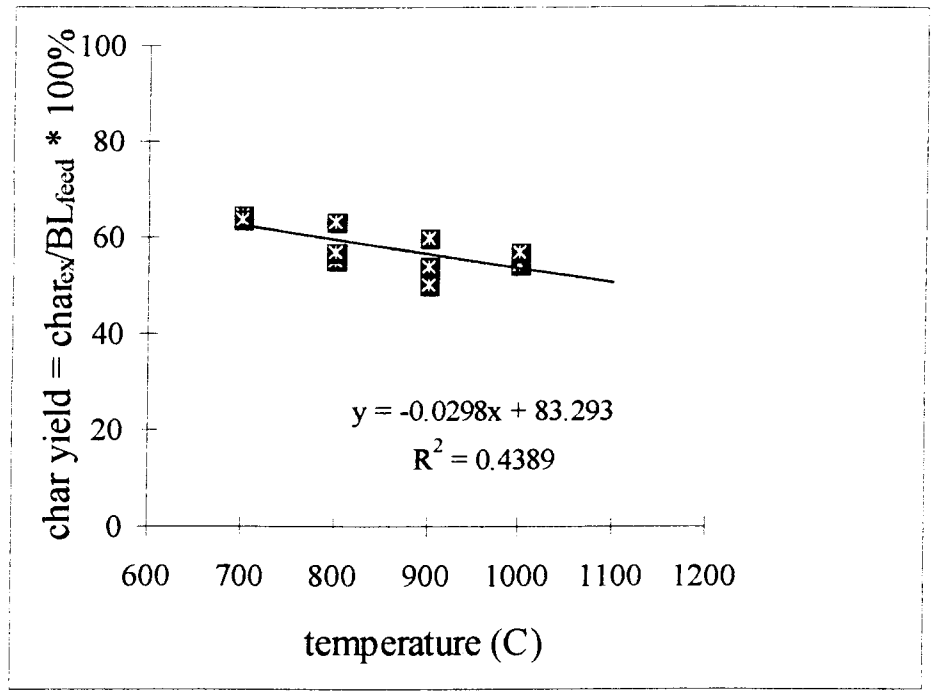


Figure E.3. Char Yield -- Feasibility Studies Using the Old Injector (residence time = varied)

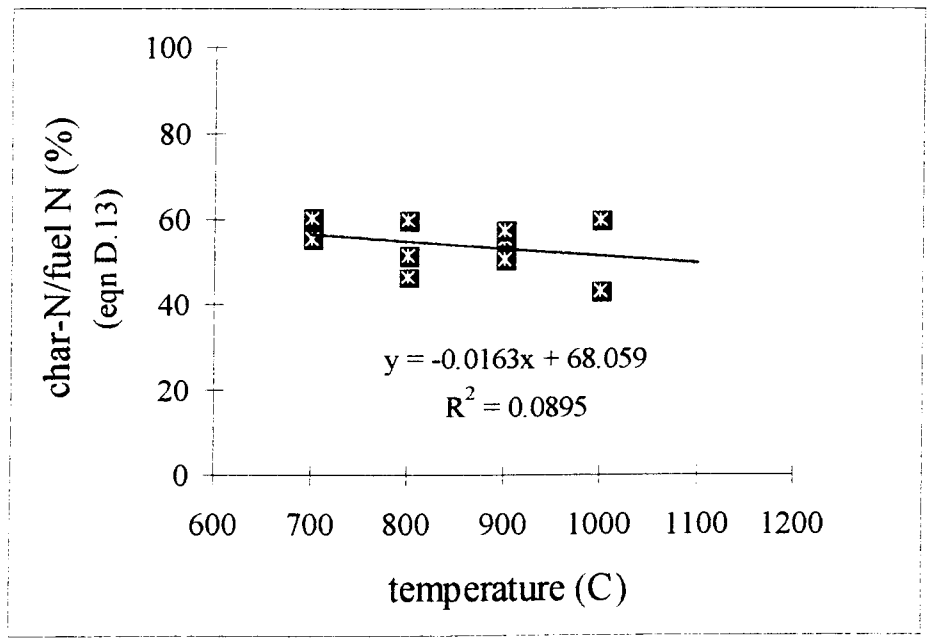


Figure E.4. Char-N Formation -- Feasibility Studies Using the Old Injector (residence time = varied)

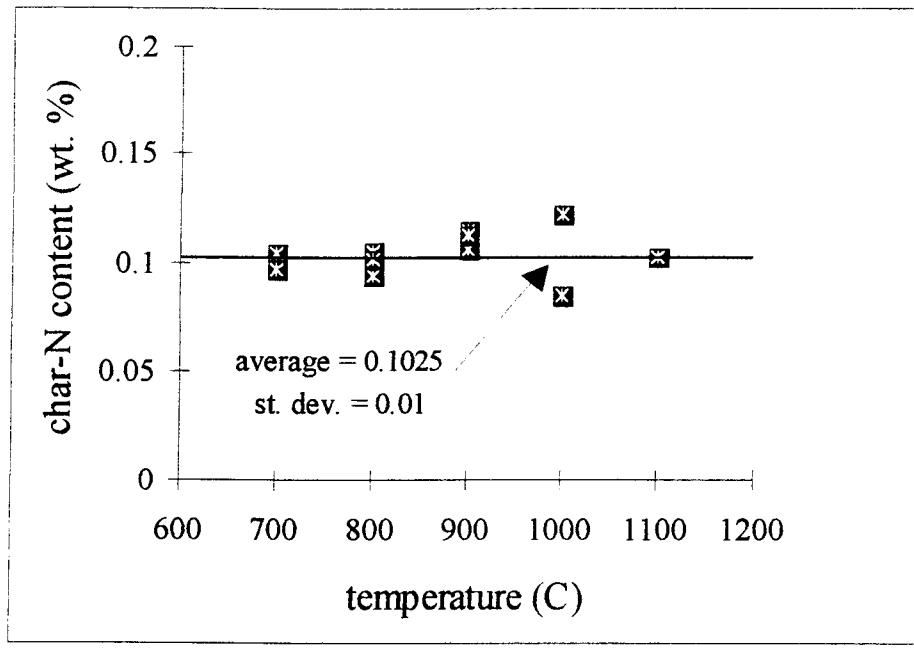


Figure E.5. Char-N Content -- Feasibility Studies Using the Old Injector (residence time = varied)

E.2 Experiments using the new injector

All succeeding experiments were made using a new injector having an inside diameter of 6.52 mm. Experiments # 26 through 44 given in **Table** A.3 in **Appendix A** were done at 900 °C. With the injector's larger diameter, the 1:1 gas velocities were maintained and the residence times were estimated more accurately. The difference between τ_p and τ ranged from near zero to about 0.1 seconds. The analytical results are included in **Table** D.3 in **Appendix D**. **Figures** E.6 and E.7 illustrates the conversion of fuel N to NO and NH_3 as a function of residence time, respectively. **Figure** E.6 shows maximum NO formation at about 1 second. The data points in **Figure** E.7 were too scattered to notice any trends in NH_3 formation.

These runs were considered good. However, the runs made in this part of the study followed the old experimental procedure. During the experiments, it was observed

that a significant amount of char exited through the collector bottom when the feed system was being flushed at high primary flow rates. Furthermore, when the injector was cleaned while the LEFR was at room temperature, a significant amount of black liquor particles was collected. The char yield and the fraction of fuel N as char-N for these experiments are plotted in **Figures** E.8 and E.9, respectively. The data points were scattered possibly because they were greatly affected by the mass loss in the feed system. The reported values of the conversion of fuel N to NO shown in **Figure** E.6 were also affected. The results on relative weight of char-N to char are reported in **Table** A.7 of **Appendix A** and are plotted in **Figure** E.10. These values were not affected by the mass loss.

With the injector's larger diameter, there were more black liquor particles accumulating on the walls of the injector. When the feed system was being flushed at the maximum primary flow rate (greater than 0.821 liters/min), the black liquor particles were knocked off the injector walls and into the reactor thus producing char and fume. To reduce the amount of mass loss, the old procedure was modified and the particulates exiting the reactor during flushing were collected by using the cyclone/filter assembly. This new procedure is the one that was adopted in the succeeding experiments. Back-flushing the injector was also included in the new procedure. The black liquor particles were not collected during back-flushing because there were no available means of doing so. However, this part of the new procedure cleans the injector for the next experiment.

The difference between the old procedure and the new procedure is best illustrated in **Figures** E.11 and E.12. The reported values using the old procedure were lower and more scattered than those obtained using the new procedure.

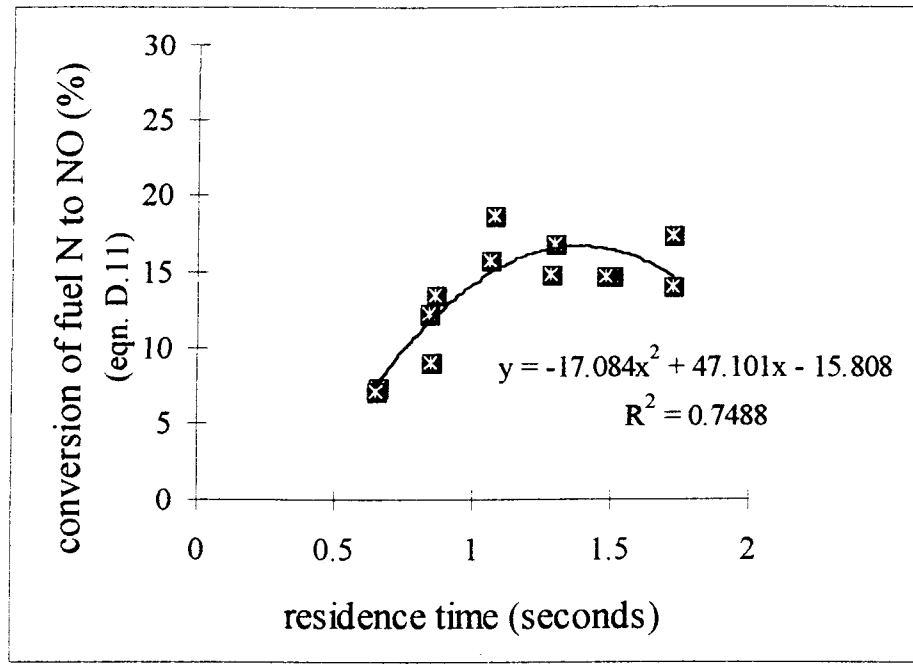


Figure E.6. NO Formation as a Function of Residence Time at 900 °C -- Old Experimental Procedure

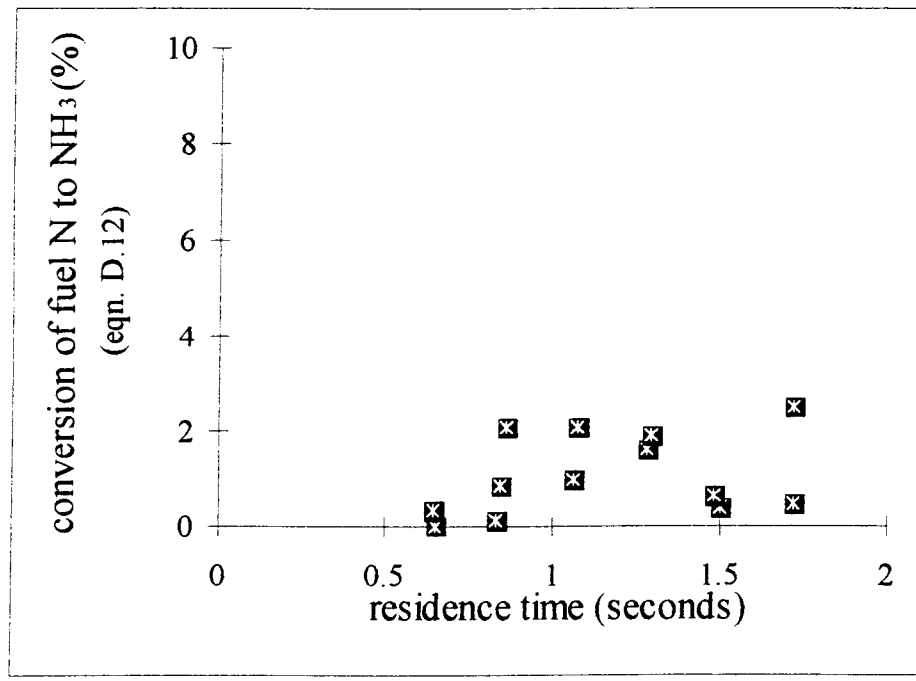


Figure E.7 NH_3 Formation as a Function of Residence Time at 900 °C -- Old Experimental Procedure

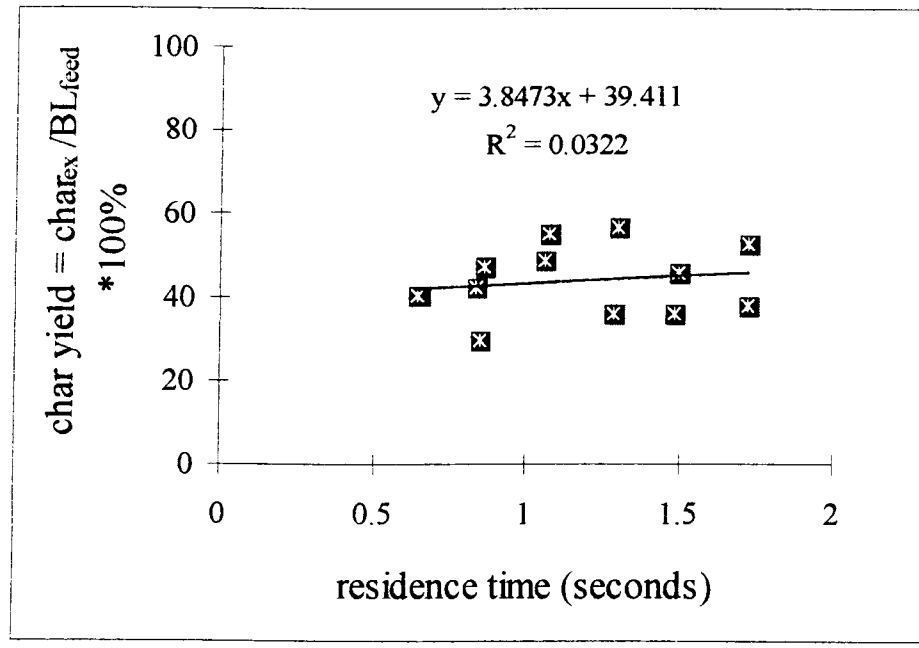


Figure E.8 Char Yield as a Function of Residence Time at 900 °C -- Old Experimental Procedure

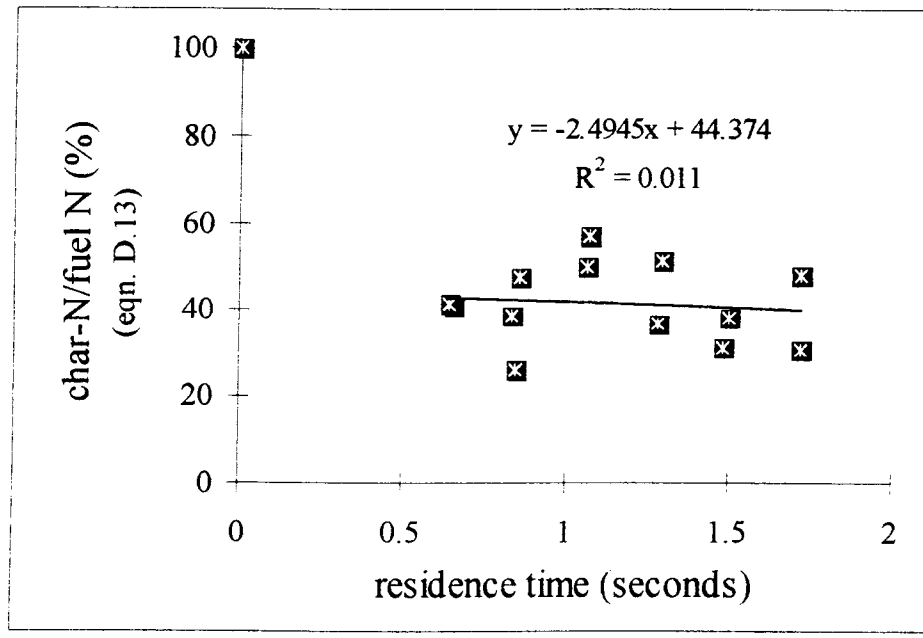


Figure E.9 Char-N Formation as a Function of Residence Time at 900 °C -- Old Experimental Procedure

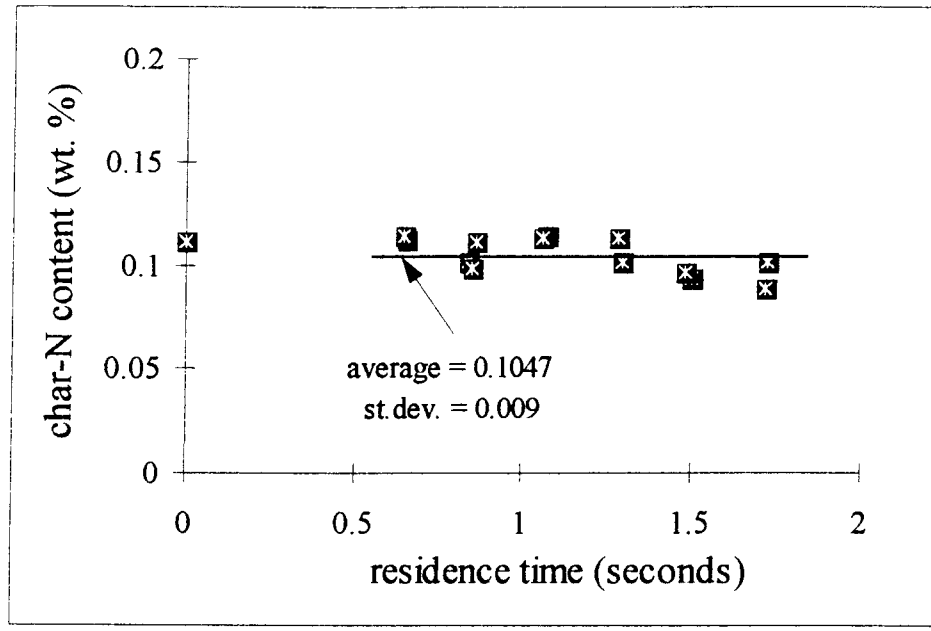
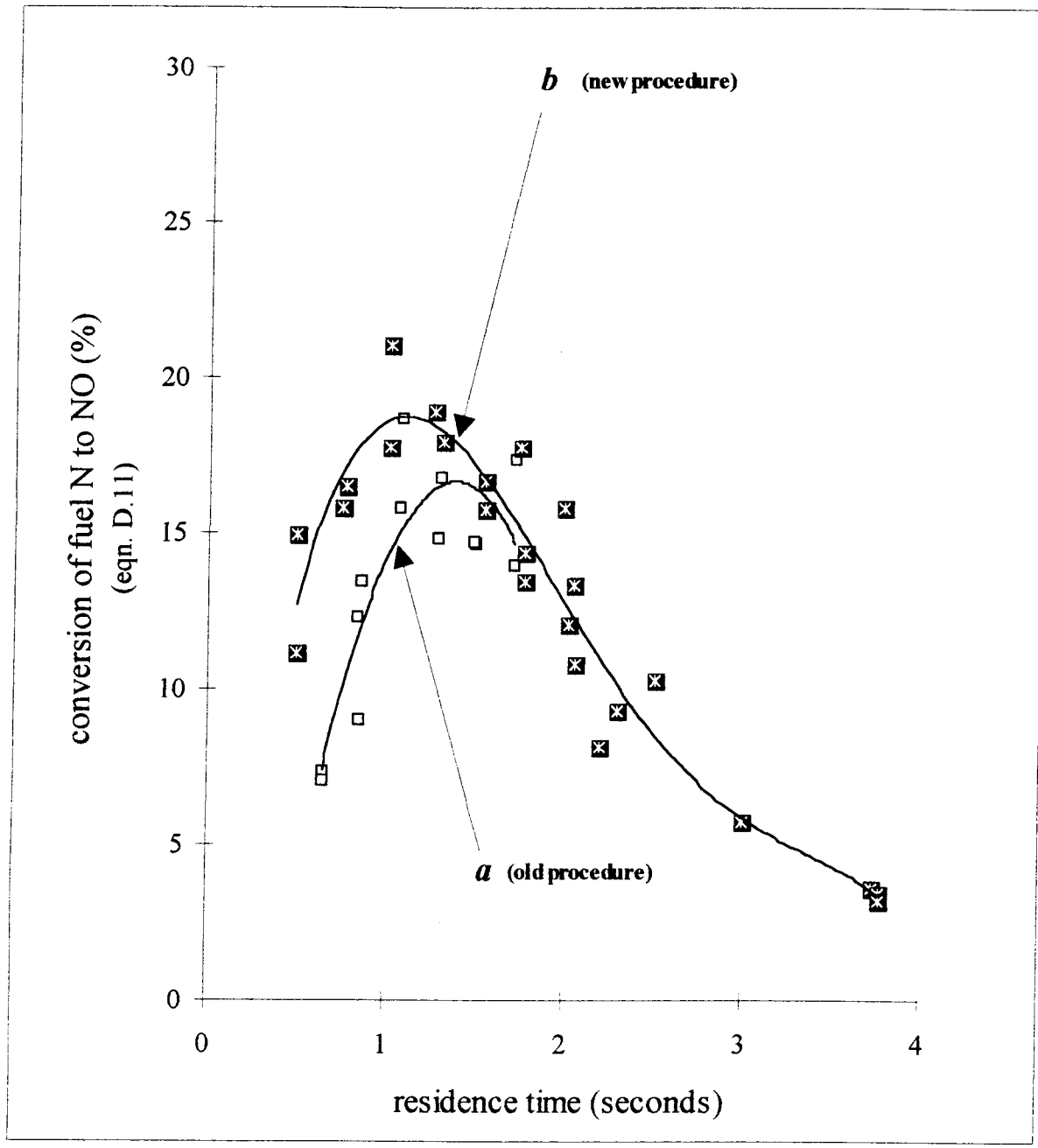
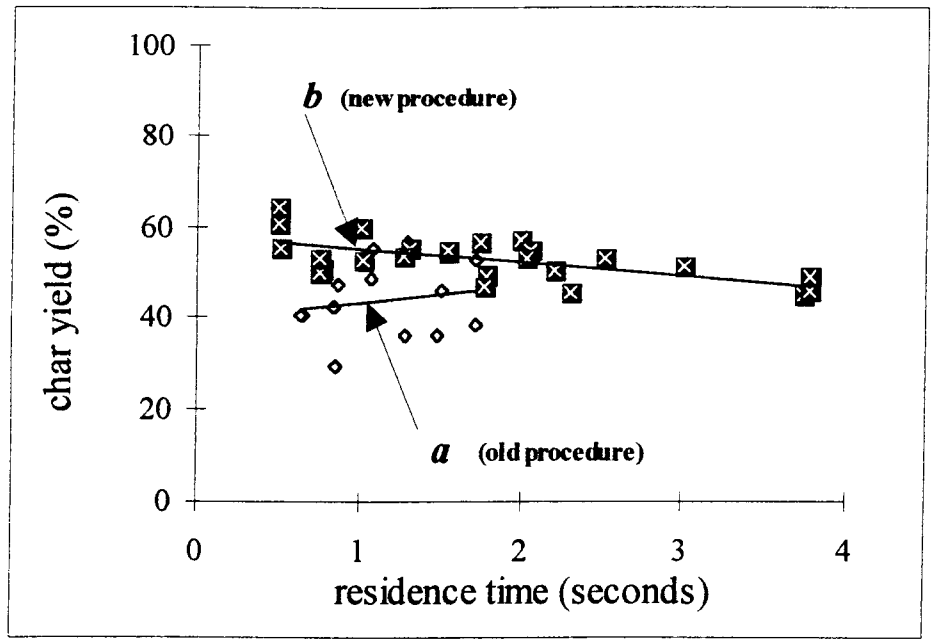


Figure E.10. Char-N Content as a Function of Residence Time at 900 °C -- Old Experimental Procedure



- **new procedure :** $y = -1.0688\,x^4 + 11.392\,x^3 - 42.189\,x^2 + 57.038\,x - 6.5474$; $R^2 = 0.9149$
- **old procedure :** $y = -17.084\,x^2 - 47.101\,x + 15.808$; $R^2 = 0.7488$

Figure E.11. NO Formation as a Function of Residence Time at 900 °C -- A Comparison of the Old and New Procedure



old procedure : $y = 3.8473\,x + 39.411$; $R^2 = 0.0322$
new procedure : $y = -2.9467\,x + 58.13$; $R^2 = 0.3806$

Figure E.12. Char Yield as a Function of Residence Time at 900 °C -- A Comparison of the Old and New Procedure

E.3 Inconsistent Black Liquor Mass Flow Rates

The mass flow rates were not constant in all the experiments. Refer to the summarized results in **Appendix D**. Although the motor speed for the particle feeder was kept constant, the mass flow rates differed from one experiment to another. The black liquor particles accumulating on the walls of the injector were restricting the flow of the black liquor solids into the LEFR. Eventually, the primary flow started to decrease and plugging occurred. The only solution to this problem was to stop the experiment and collect all data for analysis. The time at which the primary flow started to decrease was recorded in the data file analysis in **Appendix D**. This was noted as the "time at plug". In those experiments where the plugging occurred, the "time at plug" was the effective running time used in the calculations.

The change in mass flow rates may also have been due to the mass loss in the feed system. In the new procedure, the black liquor particles in the injector that were not collected in the back-flushing routine were considered to be the primary cause for mass loss. However, it has been observed that those experiments with mass flow rates greater than 0.3 g/min yield good results. Duplicate (or triplicate) experiments showed reproducible results and thus suggesting that the mass loss in the injector could be considered insignificant. On the other hand, at black liquor mass flow rates less than 0.3 g/min, there may have been important mass loss on the feed system and the experiment should be disregarded.